Thesis for the Master's degree in chemistry


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## The role of particles and phosphorus bound to particles in eutrophication

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# ABSTRACT

Phosphorus (P) transport in the eutrophic Vansjø-Hobøl watercourse is mainly associated with particles. This flux is mainly governed by soil erosion of particle bound phosphate (PP) from agricultural soils as well as in-stream and in-lake processes. While the processes governing soil erosion are rather thoroughly studied, the factors governing the formation and impact of PP in the surface waters are not well understood. Two laboratory experiments were conducted in order to investigate the physicochemical factors important for the formation and loss of PP, a sorption-desorption experiment with water and particles from the main Hobøl River and an experiment mixing forest and agricultural runoff water.

The sorption-desorption experiment demonstrated that particles from the river adsorbed $PO_4$ when they were exposed to water with elevated $PO_4$ content, increasing the P density on the particles by 35 %. When these particles were later exposed to water with low P concentration similar to the water in Lake Vansjø, about half of the sorbed P was released again within 4 days. On the contrary, no desorption of P was noted from natural particles when exposed to water containing low P concentrations. These results indicate that eroded soil particles in streams might *reduce* the amount of dissolved P. A one-sided focus on erosion-reducing abatement actions can thus be counterproductive.

Mixing acidic, aluminium rich water from a forested catchment (Dalen) with circumneutral and P rich water from an agricultural catchment (Støa) assayed the precipitation of amorphous aluminium hydroxides and its effect on the phosphorous fractionation in the mix. When using natural forest water, no precipitation of Al was observed. Increasing the concentration of monomeric Al to 26 µM and reducing the pH to 4.5 in the forest water caused Al to precipitate upon mixing with agricultural runoff water. The expected significant reduction in concentrations of dissolved P fractions and organic matter were not observed. This is believed to be due to a circumneutral pH in the water mix, causing the amorphous Al precipitates to be negatively charged and thus impeding sorption of phosphate anions and the negatively charged organic matter. These results moderate the postulation that the decrease in acid rain, causing lowered concentrations of $H^+$ and Al in forest streams, can have reduced an important sink for P in a watershed. The resulting pH of the mixed water is a key factor determining the significance of this process.

# PREFACE

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# 1 INTRODUCTION

One of the main challenges in achieving the requirements set by the EU Water Framework Directive is to reduce eutrophication caused by anthropogenic loading of nutrients from agriculture and urban activities. A water body is eutrophic when nutrient-rich conditions lead to excessive biological productivity (vanLoon & Duffy, 2011). The limiting nutrient in fresh water is usually phosphorus (P) (Dorich, Nelson, & Sommers, 1984; Pratt, 2006; vanLoon & Duffy, 2011), but several hydro-biogeochemical processes affecting eutrophication interact to make a complex overall picture.

Vansjø is a eutrophic lake in the Vansjø-Hobøl catchment south of Oslo, Norway. Considerable abatement actions to improve the water quality in Vansjø have been made, but the projected status of the lake is not achieved (Skarbøvik, Haande, Bechmann, Skjelbred, & Eggestad, 2014). This master thesis is a part of the interdisciplinary research project EUTROPIA[1], funded by the Research Council of Norway (project number 190028/S30). The project aimed to assess the impacts of changes in environmental pressures on the phosphorus mobility in the Vansjø-Hobøl catchment, which might clarify why the expected improvements have not occurred. Western Vansjø was the main study area.

Several postulations have emerged from the EUTROPIA project. A major challenge lies in linking the understanding of the mobilization processes that occur in the soil and how this affects the transport of nutrient in runoff in small streams, with the mechanisms governing water chemistry of high order rivers that drain into Lake Vansjø (Vogt, 2012). Particles flowing with the streams constitute the most important transport route for phosphorus (i.e. particulate phosphorus, PP) to Lake Vansjø, but the fate of the phosphorus bound to these particles is not adequately known: Will most phosphorus go back into solution and contribute to eutrophication once in the lake, or will it be buried with the sedimenting particles? This master thesis aims to shed light upon the processes governing formation and loss of PP, to clarify the role of particles and phosphorus bound to particles in eutrophication.

Łukawska-Matuszewska, Vogt, and Xie (2013) found that sediments originating from forested catchments are fundamentally different from sediments originating from agriculture in terms of phosphate availability. The phosphate adsorption on particles from surface runoff

[1] http://www.mn.uio.no/kjemi/english/research/projects/eutropia

and on particles from drainage pipes are also expected to be different. Stream-water samples including sediments from agricultural runoff, comprising surface runoff during storm-flow (sampled in Hobøl River) and samples mainly from drainage pipes (sampled in the Støa stream), and forested catchment (Dalen stream) are therefore studied in this thesis

A major knowledge gap lies in the understanding of sorption of phosphate to particles eroded from agricultural areas. The eroded soil material may adsorb free phosphate in the streams though this phosphate may desorb again when the material comes into the lake. For example, clay eroded through drainage pipes can adsorb phosphate in the stream due to the high concentration of free phosphate washed out from the Ap layer. In the lake, where algal activity keeps phosphate concentrations low, the equilibrium is shifted and the phosphate will again desorb. However, the total P in Lake Vansjø is much lower than what is contributed by the streams, indicating that a large amount of the particulate P (PP) must sediment without being released to the lake water (Parekh, 2012; Skarbøvik & Bechmann, 2010). This hypothesis was supported by findings of Gebreslasse (2012), studying the sediments in the streams draining into Lake Vansjø: The amount of P in stream sediments was higher than in the soil, and P concentrations in the lake sediments were lower than in both cultivated soil and in stream sediments. Thus, a one-sided focus on abatement actions reducing the soil erosion and thus transport of particles in the catchment might be counterproductive as there will be fewer particles to adsorb free phosphate in the streams. To assess these processes, sorption – desorption experiments were performed. Particles were first exposed to water with high concentration of phosphorus and then to water with low concentration, mimicking the conditions in the streams and in the lake. The sorption and desorption of phosphorus to suspended particles were measured.

The water pH affects the sorption of phosphate to particles, and modelling with PHREEQC was performed to investigate the effect of pH on sorption to particles.

Another knowledge gap regards the formation of particles where water from agricultural and forested catchments is mixed. An important hypothesis that emerged from the EUTROPIA project is that the strong decline in acid rain deposition may have been an important concurrent process disguising the effect of the abatement actions. Water in streams draining forests, covering 80% of the catchment (Skarbøvik, Bechmann, Rohrlack, & Haande, 2011), is acidic and contains labile aluminium (mainly aluminium hydroxide ions) and dissolved natural organic matter (DNOM). The DNOM inherently contains phosphate constituting a

significant amount of the background flux accounting for 39% of the total flux of phosphate to the lake (Blankenberg et al., 2008). Where a forest stream runs through an agricultural area, it mixes with water containing higher concentrations of phosphate and with a circumneutral pH. Shekobe (2012), studying the non-conservative effects of mixing forest runoff with agricultural runoff from the same streams as in this thesis, found that most of the dissolved P and the P associated with DNOM is converted into particulate bound P (PP). The mechanism is thought to be labile Al from the acid stream precipitating as amorphous oxy-hydroxides and co-precipitating phosphate. Concurrently, the DNOM precipitates due to complexation with $Ca^{2+}$ and sorbs to particles. The scale of these processes has likely decreased the last decades in the Vansjø-Hobøl Catchment as an 81% decrease in sulphur deposition (i.e. acid rain) has led to a 67% decrease in labile aluminium in lakes of south-eastern Norway. Concurrently the concentrations of DNOM have more than doubled since the 80's (Skjelkvåle et al., 2012), increasing the background flux of DNOM-bound phosphate into the lake. Experiments were performed by mixing water from an agricultural and a forested catchment and monitoring the changes in water quality to investigate the effect of the reduction in acid rain. The fate of the newly formed PP upon entering the lake was investigated by conducting a subsequent desorption study; the mixed water was filtrated, and desorption of phosphate from the original and newly formed particles was studied by exposing the filter to water from the lake with low $PO_4$ concentration. Radiochemical analytical methods were employed in the experiments to enable the determination of very low concentrations of $PO_4$.

# 2 ABBREVIATIONS

| | |
|---|---|
| **Ala** | Monomeric aluminium |
| **Alaf** | Monomeric aluminium in filtrated sample |
| **Ali** | Inorganic monomeric aluminium |
| **Alif** | Inorganic monomeric aluminium in filtrated sample |
| **Alo** | Organic monomeric aluminium |
| **Alof** | Organic monomeric aluminium in filtrated sample |
| **Alr** | Total aluminium |
| **Alrf** | Total dissolved aluminium |
| **CA filter paper** | Cellulose acetate filter paper |
| **CN filter paper** | Cellulose nitrate filter paper |
| **CPM** | Counts per minute |
| **D$^{32}$P** | Dissolved radioactive phosphorus |
| **DNOM** | Dissolved natural organic matter |
| **DOM** | Dissolved organic matter |
| **DOC** | Dissolved organic carbon |
| **DPM** | Disintegrations per minute |
| **DTP** | Dissolved total phosphorus (measured by MBM) |
| **DUP** | Dissolved unreactive phosphorus (measured by MBM) |
| **DRP** | Dissolved Reactive phosphorus (measured by MBM) |
| **GF filter paper** | Glass fibre filter paper |
| **IC** | Ion chromatography |
| **ICP-MS** | Inductively coupled plasma mass spectrometry |
| **ICP-OES** | Inductively couples plasma optical emission spectrometry |
| **LOI** | Loss on ignition |
| **LSC** | Liquid scintillation counting |
| **MBM** | Molybdenum blue method |
| **OM** | Organic matter |
| **P$^{32}$P** | Particulate radioactive phosphorus |
| **PMT** | Photo-multiplier tube |
| **PNOM** | Particulate natural organic matter |
| **PO4** | Orthophosphate, in natural waters mostly found as $H_2PO_4^-$ and |

| | |
|---|---|
| | $HPO_4^+$ |
| **PP** | Particulate phosphorus (measured by MBM) |
| **PSD** | Particle size distribution |
| **SAR** | Specific absorbance ratio; the absorbancy of a water sample at 254 nm divided by absorbency at 400 nm |
| **S filter** | Supor® filter (polyetersulfon) |
| **SRP** | Soluble Reactive Phosphorous |
| **sUVa** | Specific UV Absorbance; The absorbancy of a water sample at 254 nm divided by the concentration of DOC |
| **$T^{32}P$** | Total radioactive phosphorus |
| **TOC** | Total organic carbon |
| **TDCR** | Triple to double coincidence ratio, a quench correction method in LSC |
| **TNOM** | Total natural organic matter |
| **TP** | Total phosphorus (measured by MBM) |
| **TSS** | Total suspended solids |

# 3 THEORY

## 3.1 Biogeochemistry of Phosphorus

Phosphorous (P) is one of the main nutrients and has a predominant role in cellular energetics as adenosine triphosphate (ATP), and is usually the primary limiting factor for algal growth in fresh water. Excess supply of P to a lake or a river can therefore lead to eutrophication (Dorich et al., 1984; Pratt, 2006).

In the terrestrial compartment there are a number of minerals containing P, and it is also present complexed with Ca, Fe and Al, as a minor constituent in organic matter (OM), adsorbed to organic matter through Fe binding or adsorbed to the surface of minerals (Dorich et al., 1984; vanLoon & Duffy, 2011; Zhou, Tang, & Wang, 2005). Phosphorus (P) has no common gaseous form, and it is thus found in the atmosphere only in association with dust particles (vanLoon & Duffy, 2011). This limits the cycling of P compared to other important nutrients, such as carbon or nitrogen.

Phosphate is fractionated into total phosphorus (TP), dissolved total phosphorus (DTP), particulate phosphorus (PP), dissolved reactive phosphorus (DRP) and dissolved unreactive phosphorus (DUP) (see Chapter 4.3.1.4). These fractions are in equilibrium with each other, and the equilibrium can change depending on water quality, as discussed in Chapter 3.2. TP is often used as an indicator for the ecological quality of a lake, even though it is the biological available fraction that is important. However, the TP is usually strongly correlated with bioavailable phosphorus. The concentration of DRP, constituted mainly of free orthophosphate species, is used as an estimate for how much P that is bioavailable (Ekholm, 1994). Dissolved reactive P in river waters appeared to be totally bioavailable whereas the dissolved unreactive P appeared not to be utilized by algae (Ekholm, 1994). There are though arguments that DRP is not a good indicator for what is in fact biologically available (McKelvie, Peat, & Worsfold, 1995). PP seemed to mainly become bioavailable by desorption (Ekholm, 1994). The conditions allowing desorption of P - like the dissolved P concentration – can be investigated by sorption-desorption experiments. DUP includes the organically bound P, which can become bioavailable over time.

## 3.2 Processes governing phosphorous fractions in water

The mobility of P in water is mainly determined by solubility reactions and adsorption to particles.

### 3.2.1 Phosphorous solubility

Phosphoric acid, the fully protonated orthophosphate species, has $pK_a$ values of 2.15, 7.09 and 12.32 (O'Neil, 2012c). The dominating free orthophosphate species are therefore $H_2PO_4^-$ or $HPO_4^{2-}$ at the pH found in most natural waters, and these will in the text be referred to as $PO_4$. The limitations in phosphate availability are related to the insolubility of important phosphate salts (Pratt, 2006). $Fe^{3+}$ and $Al^{3+}$ forms insoluble compounds with $PO_4$ species below pH 4.5, and $Ca^{2+}$ above pH 7 (vanLoon & Duffy, 2011). This controls the solubility of $PO_4$ in water and leaves only a small pH region where significant concentrations of orthophosphate ions can be found in most freshwater. Maximum solubility will be obtained by slightly acidic conditions, which is what is found in most Norwegian lakes (Skjelkvåle et al., 2012).

When the system becomes anaerobic, $Fe^{3+}$ is reduced to $Fe^{2+}$. Sulphate is also reduced, trapping Fe as FeS (O'Neil, 2012a, 2012b; Pratt, 2006), in turn releasing phosphate (Gächter & Müller, 2003). The binding of $PO_4$ to Fe is therefore highly susceptible to changing redox conditions. Oxic lake sediments are found to retain phosphate more efficiently than anoxic sediments, and the sediments can release large amounts of phosphate when becoming anoxic, due to iron no longer binding phosphorus. Olsen (1958) did laboratory experiments with sediments in reducing and oxidizing conditions, and found a much higher adsorption under oxidizing conditions, as expected.

### 3.2.2 Phosphorus sorption

The desorption of phosphate anions from suspended particles increases as pH increases and surface charge becomes more negative (Zhou et al., 2005). The surface charge of a solid is the sum of structural deficits, unbalanced bonds at the crystal surface and charge generated by the adsorbed ions (Appelo, 2010). The charge due to structural deficits and unbalanced bonds at the crystal surface is independent of pH, while the charge generated by the adsorbed ions is dependent of pH. At a given pH, the proton charge will compensate all other charge. This pH value is called the point of zero charge (PZC).

The charge of a solid is balanced by the diffuse double layer (Appelo, 2010). The diffuse double layer is an increased concentration of oppositely charged ions surrounding the clay mineral, which again is balanced by counter ions.

Elevated pH can occur in a lake during periods of high algal growth, and cause increased desorption and thus availability of P. Ekholm (1994) did sorption experiments by pH 7 and pH 9. These pH values corresponds to pH when a lot P is added to lake (like autumn storm) and by algal growth (summer). Adsorption was found to be much lower by pH 9 than by pH 7.

Aluminium is a strong precipitating agent for dissolved organic matter (DOM). This is utilized in water treatment where DOM is coagulates by destabilizing the humic matter (Eikebrokk, 2012). The raw water is added $Al^{3+}$ which precipitates as aluminium oxy-hydroxides. These particles have positive surface charge at pH below 6.3 and thus sorb the negatively charged DOM. The pH of the water during the removal of the particles is therefore important as it dictates the solubility and charge of the Al precipitates; above pH 6.3 the Al hydroxides become more soluble, are mainly negatively charged and will therefore not act as a coagulant for the negatively charged material (see Figure 3-1). Moreover, addition of aluminium ions are used in a similar manner in sewage treatment plants to precipitate out the orthophosphate. The phosphorous is both sorbed to the amorphous aluminium oxy-hydroxides and precipitates out as aluminium phosphate.

Aluminium and iron are also important for sorption of $PO_4$ to soil as the polyvalent ions acts as a charge bridge between net negatively charged soil surfaces and DNOM, and the phosphate anion.

## 3.3 Factors affecting transport of phosphorus in a catchment

### 3.3.1 Dissolved organic bound phosphorous

South-eastern Norway, were the Vansjø-Hobøl catchment is located, has the highest concentrations of total organic carbon (TOC) in Norway with some lakes having concentrations of 15-20 mg C $L^{-1}$ (Skjelkvåle et al., 2012). TOC is a measure for total natural organic matter (TNOM), and the approximate relation between the two is TNOM ≈ 1.7 × TOC (vanLoon & Duffy, 2011). In the contributing streams of Western Vansjø,

concentrations of 4 to 23 mg C $L^{-1}$ is found (Parekh, 2012). Transport of organic matter inherently leads to transport of P. This is one of the main natural sources of P to water systems, and in 2005 the background flux of P was estimated to account for 39 % of the P flux to Vansjø (Blankenberg et al., 2008). TOC in Norwegian water systems have more than doubled the last decades, due to decreased anthropogenic sulphur deposition (de Wit, Mulder, Hindar, & Hole, 2007; Haaland, Hongve, Laudon, Riise, & Vogt, 2010; Monteith et al., 2007; Skjelkvåle et al., 2012). The solubility of especially large molecular weight organic particles increase when pH is increased and the ionic strength is decreased (by the reduction in the leached ions and sulphate) (vanLoon & Duffy, 2011), and thus a decrease in acid rain leads to increased solubility of organic matter (OM). The acid rain reduction might also have had an indirect effect on the TOC concentrations by causing the Al leaching to be reduced. As discussed in Chapter 3.2.2, labile Al can precipitate organic matter by flocculation, but more important is the reduced amount of OM that goes into solution from the soil.

An important property of OM is that it readily forms strong complexes with metal cations, especially trivalent ions such as aluminium and iron (Gerke, 1993). As described in Chapter 3.2.2 the Al and Fe form charge bridges that bind phosphate to the negatively charged dissolved natural organic matter (DNOM). This increases the solubility of $PO_4$ and thereby contributes to the transport of P beyond what is structurally a part of the DNOM. OM is also important for binding between clay particles and phosphate, as is further discussed below. Gerke (1993) observed that addition of humic substances to Fe oxides increases the absorption of P.

One hypothesis that has emerged from the EUTROPIA project is that the increased leaching of DNOM due to the reduction in sulphur deposition has led to an increased background flux of P to the lake, an effect that might have contributed to disguise the effect of the abatement actions that have been carried out.

### 3.3.2 The role of particle bound phosphorous

The total phosphorus content of natural waters comprises both particulate and dissolved forms, the former being operationally defined as the fraction which does not pass through a 0.45 µm membrane filter. Phosphorus associated with particles (PP) comprise material of biological origin, weathering products, inorganic precipitates, organic and inorganic co-precipitates and

organic aggregates, as well as P associated with aggregates through metal binding or adsorbed to the surface of clay and mineral particles (McKelvie et al., 1995).

Phosphorous bound to particles constitute the main fraction of total phosphorous that is transported to lake Vansjø (Parekh, 2012). The temporal and spatial variation in transport of P associated with particles is mainly governed by runoff intensity and land use in a watershed (Munn, McLean, Ramirez, & Logan, 1973; Parekh, 2012). Even though orthophosphate bound to particles constitute the main fraction of total phosphate transported to Vansjø, it might not contribute as much to eutrophication as its amount indicates (Vogt, 2012). The potential bioavailability of P in agriculturally loaded rivers in Finland has been determined by an algal bioassay and the release of potentially bioavailable PP was estimated by sorption studies (Ekholm, 1994). According to the bioassay 0 to 13.2 % (mean 5.1 %) of the particulate P in river water samples was potentially bioavailable (Ekholm, 1994). Two lake sediment samples were also assayed. In the sediment material, 2.6% of the P was bioavailable and the P in the lake bottom sediment sample was not utilized by the algae at all (Ekholm, 1994). The potential bioavailability of PP in agriculturally loaded rivers obtained in this study was lower than that reported in studies from other countries.

Only a small fraction of the phosphate associated with particles is or may become bioavailable, and eroded clay particles may on the contrary scavenge free phosphate from a stream, as clay particles have very high adsorbing capacity (Dorich et al., 1984). Particles entering the lake will sediment, and these particles can either sorb or release P in the water before sedimentation. The fate of phosphate associated with particles is thus so far not satisfactory understood, and abatement actions that aim to reduce the particle transport to Lake Vansjø might even be counterproductive.

Different sorption processes govern the capacity of particles to accumulate P and thereby the distribution of different P pools in the particles. The most important sorbing properties of the particles are surface charge and area. These properties are mainly controlled by the content of clay, organic matter and metal (Fe, Al) oxides and hydroxides (Detenbeck & Brezonik, 1991a; Zhou et al., 2005). Clay is important for sorption due to the large surface area. Iron and aluminium constitute charge bridges between negatively charged clay particles or OM, and the phosphate anion. The P adsorption capacity depends therefore on the chemical composition of sediments as well as the ambient redox conditions, pH and ionic strength (Detenbeck & Brezonik, 1991a; Gerke, 1993; Łukawska-Matuszewska et al., 2013). Ionic

strength is important as the other ions in solution will compete for sorption sites on the particles. pH is as noted above important for the sorption of phosphate to particles, but particle composition have however been found to be more significant than pH in affecting P sorption in natural sediments (Zhou et al., 2005).

Different studies have found that as much as 95 % of P in cropland run-off is associated with the particle phase (Dorich et al., 1984; Parekh, 2012). The total P concentration in run-off is therefore found to be directly related to the proportion of fine particles, as fine particles have greater surface and thus greater sorption potential. The concentrations of P in eroded materials are also greater than the concentrations of P in the surface soil (Gebreslasse, 2012). This may indicate that components of soil high in P are selectively eroded – which is not unexpected as smaller particles can more easily flow with the water. However, it can also mean that phosphate is sorbed to particles in the stream. These fine materials may remain in the photic zone of lakes for extended periods, increasing the time for a new equilibrium to establish, which may include desorption of PO4 to the water as the PO4 concentration in a lake is normally lower than in the agricultural stream due to grazing by algae.

When suspended particles contacts with water, PO4 will be exchanged with the water on the interface until a dynamic equilibrium is reached. Models that are often used to describe such equilibriums include the empiric Langmuir relation and the Freundlich relation (vanLoon & Duffy, 2011). Different fractions of PO4 will exchange more or less easily, and as aging increases the binding of P to the particles, newly sorbed P will generally desorb more easily.

### 3.3.3 Effects of Land use and Climate on erosion

Different land use in the watershed is an important explanatory factor for the spatial variation in transport fluxes of P to the water system (Munn et al., 1973; Parekh, 2012; Skarbøvik et al., 2014). Specifically, land use distribution and runoff intensity have been found to greatly influence the concentration and composition of P fractions in rivers draining into Vansjø. Median concentration of total P in nine studied streams draining to Lake Vansjø varied from 0.3 to 3.1 µg/L (Parekh, 2012). PP constitutes 35 % to 80 % of the TP in the investigated streams. The total P concentrations show increasing trend with increasing proportion of agricultural land in the watershed of the streams. This is due to long term excess use of fertilizer making agricultural soils more P rich and enhanced erosion, especially during

periods without vegetation cover. Slope and soil texture are also important factors controlling erosion.

Precipitation and winter temperature directly effects the erosion of soil. Intensity and amount of rainfall controls the run-off flow velocity, and high run-off gives high particle transport. Autumn rainstorms, winter mild-spells and spring snowmelt are important periods of P transfer from land to water. Opland (2011) showed through flux estimations that as much as 23 % of the total P load to Vansjø for the hydrological year 2010 may have been released during only four days (31.03.10 – 03.04.10). Winter snowmelt episodes carry a greater amount of P than runoff events during other seasons, likely due to lack of vegetative cover where fall tilling is practiced and reduced water infiltration capacity of the frozen soils. There is also no primary production in the winter; therefore, the mobilized free phosphate will not be assimilated and will therefore be allowed to migrate freely. Weathering by freezing and thawing also makes the soil more susceptible for erosion (Skarbøvik et al., 2014; Williams & Smith, 1989). Inter-annual variation in winter temperature around 0°C has thus been found to be an important factor that may govern the variation in inter-annual flux of P (Parekh, 2012).

Precipitation amount and winter temperatures in the Vansjø-Hobøl catchment has been higher than normal the last decades (Skarbøvik et al., 2011). These changing weather conditions have had a large influence on the Hobøl River (the river chosen to represent the watershed, which also contributes the greatest part of P to Vansjø) as increased water flow in the river bring about erosion of the river bank, giving increased transport of particles with a lot of P to Storefjorden. Furthermore, the increased amount of precipitation leads to more waterlogged soil which can experience reducing conditions leading to release of P due to the reduction of iron (see Chapter 3.2.1). The large flood in year 2000 gave thereby negative impacts on Lake Vansjø that the lake is still recovering from.

The reduction in acid rain loading combined with the higher precipitation and winter temperature might therefore explain the slow restoration of Lake Vansjø despite the considerable concurrent abatement actions.

Drainage pipes are found to be an important transport route for P from soil to surface waters (Opland, 2011). This is partly due to erosion of P rich marine clay soil around the pipes and also because the water leaking into the drainage pipes is flushed down from the Ap horizon through macro pores in the soil. This Ap horizon soil water, which is rich in phosphorous, has less time to equilibrate with soil which could have caused sorption of P to the soil. The high

velocity of the water in the drainage pipes also allows the water to transport a greater amount of particles.

As noted above; massive amounts of particulate bound P is fed into Lake Vansjø from tributary streams, and particulate P is the greatest contributor to the total P flux to the lake (Parekh, 2012) . However, little of this PP is actually found in the lake water (Gener, 2010). This may indicate that PP does not contribute as much as its amount indicates to the total P in the lake as it is largely sedimented. One-sided focus on reducing particle transport to the lake may on the contrary lead to more bioavailable P, as less P is scavenged by particles entering the lake, and less particles are sedimented to cover newly sedimented particles and biomass from the lake. This can give more P available for re-suspension and increased internal loading in the lake. Mitigation measures aimed at reducing erosion may therefore actually be counterproductive in alleviating the eutrophication problem in Lake Vansjø. This hypothesis has emerged in the EUTROPIA project.

Several actions are taken to reduce erosion and inherent P losses worldwide, like reduced tillage, contour cropping, establishment of vegetation buffer strips in riparian zone and construction of settling ponds and wetlands (Ekholm & Lehtoranta, 2012). Actions like these are also taken in the Vansjø – Hobøl watershed (MORSA, 2014). Unfortunately, reduced tillage can increase the amount of free P in the upper layers of soil, and also the amount of free P in the runoff (Ekholm & Lehtoranta, 2012). Thus, decreasing the amount of particles that can adsorb free P and at the same time increasing free P can lead to increased availability of P in a lake, while the erosion-reducing actions were taken to achieve the opposite.

### 3.3.4 Effect of reduced acid rain loading on P mobility

There has been an 81 % reduction in sulphur concentrations in lakes in the south-eastern part of Norway since 1980. This is due to reduction in the acid rain loading, of which sulphuric acid is the main active component (Skjelkvåle et al., 2012). The reduction in sulphur concentrations has led to a 67 % decrease in labile Al concentrations in the lakes (Skjelkvåle et al., 2012). The main reason for this decrease is the reduction in $SO_4^{2-}$ as a mobile counter ion for $Al^{3+}$.

It has therefore been postulated in the EUTROPIA project that reduced aluminium leaching in the runoff from forested catchments has reduced an important removal process of phosphate in the streams draining to Vansjø (Parekh, 2012; Vogt, 2012): Streams from forested

catchments often contain high concentrations of dissolved organic matter (DOM), and when the area is influenced by acid rain it can also contain significant amounts of labile aluminium ($Al^{3+}$). The DOM inherently contains an amount of P constituting a significant background source of P to the lake. Where the stream runs through an agricultural area, it mixes with water of neutral pH and containing higher concentrations of phosphate. The $Al^{3+}$ from the acid stream then precipitates as amorphous oxy-hydroxides and co-precipitate phosphate. The scale of $Al^{3+}$ removal process of dissolved phosphate has likely decreased the last decades as the leaching of Al has decreased. In addition, the DOM will also precipitate due to complexation of $Ca^{2+}$ or sorption to particles.

In a preceding study (Shekobe, 2012) a mixing experiment was conducted where water from a stream draining agricultural area (Støa1) was mixed with water from a stream draining a forested catchment (Dalen). Both streams are from within the Vansjø-Hobøl catchment (see Figure 4-1). The mixing was meant to simulate what happens in streams as described in previous paragraph, and the concentration of several chemical parameters were monitored to observe the effect. Both Al and phosphate was lost from solution.

This precipitation of phosphate with aluminium has likely decreased due to the reduction in leaching of aluminium to streams from acid-sensitive, forested catchments. Several articles supports a theory of oligotrophication of lakes due to acidification (Detenbeck & Brezonik, 1991b; Olsson & Pettersson, 1993; Stockner, Rydin, & Hyenstrand, 2000), a theory suiting the EUTROPIA theory that a decline in acid rain have led to increased transport of DNOM and P to Lake Vansjø, increasing the eutrophication problem.

The charge of the monomeric aluminium (the species depicted in Figure 3-1) is determined by pH, and is important for the behaviour of pH in natural waters.

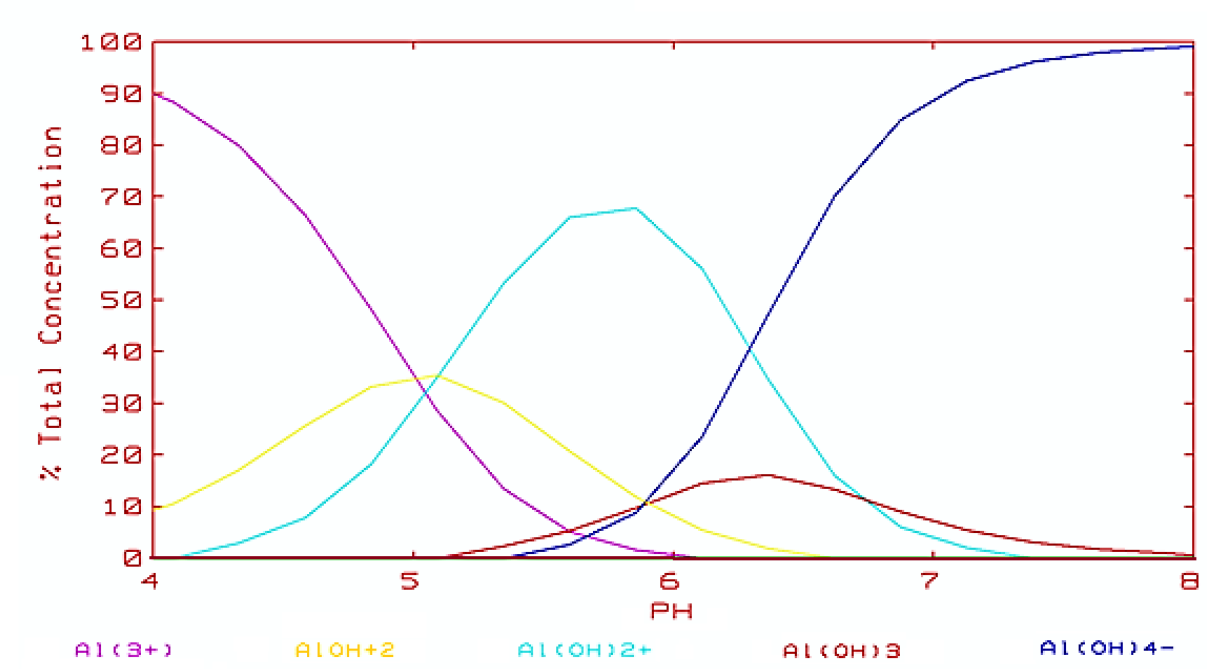


*Figure 3-1: The charge of Al in solution is dictated by the pH. This affects the solubility of the Al, and its properties towards binding with negatively charged phosphate and OM.*

### 3.3.5 Internal loading of Phosphorus from Sediments

Input of P to a freshwater system can be allochthonous or autochthonous. Lake restoration from eutrophication can be significantly delayed by P released from the sediments (Søndergaard, Jensen, & Jeppesen, 2001). The dynamics, controls and effects of P sorption in sediments are still incompletely understood, although it has been the topic of many previous studies (Zhou et al., 2005). Increasing the understanding of the processes governing the exchange of bio-available P across sediment-water interface is of major importance (Łukawska-Matuszewska et al., 2013).

The concentrations of P in sediments in Vansjø have been found to not be especially high (Andersen & Færøvig, 2007). The P in the sediments in the shallow parts of Western Vansjø seems to be quite dynamic, and releases likely P to the water column in the summer when the plant growth is highest and thus the SRP concentrations lowest, but the P comes back to the sediments during the autumn. However, the study concluded that there is likely not enough P to contribute to internal loading many years after external P loading is sufficiently decreased.

A study carried out in Sæbuvannet, a small eutrophic lake in the watershed of Vansjø (Łukawska-Matuszewska et al., 2013), obtained results that implied that sediments may in periods be a source of P, but in overall may tend to scavenge particles from the water. This depends on the concentration of soluble reactive phosphorous (SRP) in the lake water. In the dormant period, there are higher concentrations of DRP in the water, and the sediments may tend to scavenge P.

In Sæbuvannet it was also found that differences in land-use in the catchment had strong impact on the geochemistry and sorptive properties of sediments (Łukawska-Matuszewska et al., 2013). P in sediments of estuaries of agricultural influenced rivers was bound stronger than P in estuaries of forest streams, and the estuaries of forest streams can thus be a substantial source of P during re-suspension events. If the sediments contain P bound to Fe(III), this is a potential important source of P under anoxic condition.

## 3.4 Sorption – desorption studies

Information on the release of P under different chemical conditions is obtained from sorption-desorption experiments (Ekholm, 1994). On the basis of P isotherms it is possible to estimate the P concentration range where the desorption of P is possible.

Łukawska-Matuszewska et al. (2013) found different P fractionation and sorption properties for sediments sampled in different parts of Lake Sæbyvannet, in the Vansjø-Hobøl catchment. Especially, there where big differences in sediments by the inlet of agricultural and forested rivers, with several times more labile adsorbed phosphorus in the sediments by the inlet of the forested streams. This suggests that one-sided focus on reducing erosion (with abatement actions performed in agricultural areas) might not have the desired effect on the eutrophication and P-levels in Lake Vansjø.

Olsen (1958) also found big differences in the sorption properties of sediments from different parts of the lake. In general, the variation in P sorption was large, from 5 to 20-30 000 µg P per g particles for different sediments and standard materials.

## 3.5 Water-mixing experiments

Shekobe (2012) performed water-mixing experiments with water from the same two streams as are used for water-mixing experiments in this thesis. Removal of up to 90 % of $PO_4$ as Al precipitated was observed when natural water from the two streams were mixed, suggesting this as a very important process for removal of $PO_4$ in a watershed.

Liming of rivers has been done to reduce the detrimental effects of Al leaching on fish stocks due to acid rain. Where a limed river – with neutral pH and high Ca concentrations – mixes with a not-limed river with low pH and high Al concentrations precipitation of Al occurs (Lydersen, Salbu, Polèo, & Muniz, 1991; Rosseland et al., 1992). Monomeric, inorganic aluminium (measured in this thesis on filtrated samples, and thus named Alif) is rapidly polymerized and forms colloids, in the form of amorphous hydroxyl-aluminium complexes ($Al(OH)_3$) (Hem & Roberson, 1967). The initial rate of precipitation is thought to be in order of seconds, while a slower process of continuing formation of polymers continues for several hours (Lydersen et al., 1991). The colloids are relatively inert and therefore not measured by the method of Barnes (1975) and Driscoll (1984) used for the measurement of monomeric Al. The dissolution of amorphous $Al(OH)_3$ was found to be order of magnitudes slower than the formation of amorphous $Al(OH)_3$. Rosseland et al. (1992), investigating the mixing zone between streams, observed no significant changes in the organic monomeric aluminium (here named Alof).

## 3.6 Liquid Scintillation Counting

A radioactive phosphorus isotope, $^{32}P$, was used in the water-mixing experiments to achieve a low detection limit for P. $^{32}P$ is a high energy β emitter, and is easily detected with liquid scintillation counting (LSC). LSC is a detection method based on certain compound's ability to emit light if excited by radiation (Loveland, 2006). The light-emitting compound ("scintillator") and the sample are mixed together in a scintillation cocktail. This eliminates all problems with self-absorption and in addition provides nearly 100% detector geometry. The emitted light is then measured by sensitive light-detectors placed outside the vial containing the scintillation mixture, commonly referred to as a scintillation cocktail. This method of radiation detection is generally named Liquid Scintillation Counting (LSC), and is in many cases the best technique for detection and measurement of α and β radiation. The cocktail consists mostly of non-scintillating solvent molecules. The radioactive material that is to be

measured excites solvent molecules which transmits the excitation to scintillator molecules. These then emit light when they relax.

# 4 MATERIAL AND METHODS

## 4.1 Study area: The Vansjø-Hobøl catchment

The Vansjø-Hobøl catchment (Figure 4-1) is a nutrient rich, low-lying water system with more than 90 % of the area lying under the marine limit (Skarbøvik et al., 2011). P rich, marine clay containing apatite is generally found in the valley bottom and the low-land plains (Desta, 2013). The catchment is totally 688 $km^2$, with 15 % of the area used for agricultural purposes and the rest of the area being mainly forest (Skarbøvik et al., 2011).

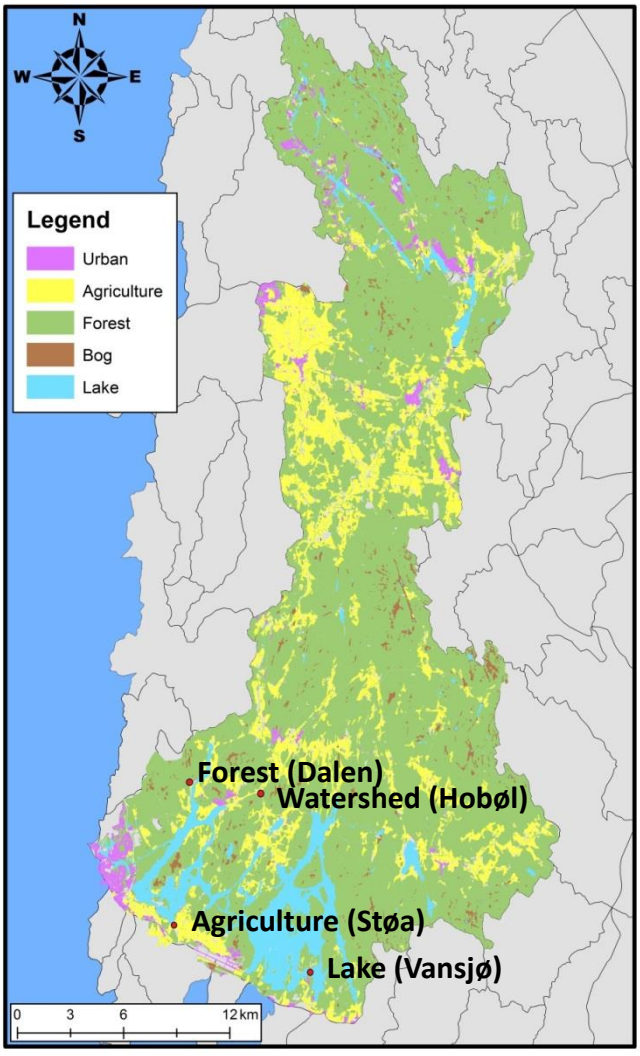


*Figure 4-1: The Vansjø-Hobøl catchment with land use. The four sampling points are marked. Credits: Christian Wilhelm Mohr.*

Lake Vansjø has a surface area of 36 $km^2$, but consists of several pools separated by narrow straits and shallow thresholds (Skarbøvik et al., 2011). Here, Lake Vansjø is considered as divided in two main basins; the eastern Storefjorden with an area of 24 $km^2$ and Western Vansjø, covering 12 $km^2$. Western Vansjø is shallow with an average depth of only 3.7 m, and it is also the most eutrophicated part of Vansjø, and the main study area of the EUTROPIA project ("EUTROPIA," 2014). Being shallow, Western Vansjø is more susceptible to re-suspension of sediments, and desorbed phosphorus can more easily reach the photic zone. Most of the contributing rivers drain into Storefjorden which flows into Western Vansjø. The outlet of the lake is by Mosseelva (the Moss River) draining from Western Vansjø.

In the period 2005-2013, Storefjorden received an estimated average amount of 17 tons of phosphorus, of which 9 tons were retained in that part of the lake and 8 tons were transported to Western Vansjø (Skarbøvik et al., 2014). Western Vansjø also received 3 tons from the local watershed. 1 ton phosphorus was retained in Western Vansjø, and the rest (10 tons) were transported with the Moss River.

Considerable abatement actions have been made to reduce the eutrophication in Lake Vansjø, but the P levels have not decreased as much as expected. Earlier studies (Mohr, 2010; Skarbøvik & Bechmann, 2010) have given changes in environmental pressures as the likely reason. This includes changes in climate, land use (due to intensification of the agriculture) and long-range transported pollutants (reduction in acid rain leading to decreased Al leaching and increased flux of DNOM, as discussed in Chapter 3.3.3).

The water quality in Western Vansjø has improved slightly the last years. During the last 9 years the concentration of total P has decreased, reaching a level that has not been lower since 1989, and the amount of algae is reduced (Skarbøvik et al., 2014). This can probably partly be explained by a decreasing supply of P from the agricultural streams around the western basin, as a number of abatement actions aimed at reducing the flux of P to the lake have been conducted in this part of the catchment. However, the improvement can also just be a recovery after the big flood in 2000 (Orderud & Vogt, 2013; Skarbøvik et al., 2014). Phosphate, on the other hand, has increased, and in Storefjorden there seem to be increases in both total phosphorus and DRP.

Agriculture contributes 57 % of the total P loading to Vansjø, while 17 % comes from sewers and the natural background loading accounts for 26 % (Solheim et al., 2001).

As a part of the Eutropia project 9 streams in the Vansjø-Hobøl catchment have been studied (Gebreslasse, 2012; Parekh, 2012), and among these 2 streams were chosen for this study to be examples of a stream from a purely agricultural catchment (Støa) and a stream draining a purely forested catchment (Dalen). In addition, a stream representing the watershed as whole (Hobøl) was chosen. The sampling sites are however not necessarily generic examples of such. Water was also sampled from Storefjorden, at Oksenøya, representing the lake.

### 4.1.1 Watershed stream (Hobøl)

The Hobøl River was chosen to represent the watershed as a whole as it drains about half of the watershed, contributing 60 % of total phosphorus (TP) to Vansjø in the hydrological period from October 2012 to October 2013 (Skarbøvik et al., 2014), and as it has a land use distribution similar to the whole watershed with 79 % forest and 16 % agriculture (Skarbøvik & Bechmann, 2010). The Hobøl River drains to Storefjorden (see Figure 4-1).

The river is a very turbid stream as it flows through areas with high clay content. The river contain about 120 mg $L^{-1}$ suspended particles during high discharge (Gebreslasse, 2012) and 10 mg $L^{-1}$ at low flow. There have been big soil slides around the river (e.g. in 2008), greatly affecting the transport of P to Vansjø (Skarbøvik et al., 2014).

From 1985 to 2013 the year average TP concentration in Hobøl (not corrected for variations in water discharge) varied between 1.4 and 4.8 µM P (Skarbøvik et al., 2014). In the same period, there is a probable down-going trend in the TP ($p = 0.13$) and total nitrogen (TN) ($p = 0.18$) fluxes corrected for water discharge (Skarbøvik et al., 2014). Monitoring data from 1985 to 2013 shows that the yearly flux of total phosphorus (TP) and total suspended solids (TSS) in the Hobøl River are closely correlated suggesting that particles and thus erosion in the watershed is important for the transport of TP to Vansjø (Skarbøvik et al., 2014). Investigating the correlation between water flow and TP shows that after the flood in year 2000 less P has been transported by a given water flow compared to the period 1985-1999, indicating an reduced risk of P loss in the watershed. This can have been a consequence of that the flood flushed out a lot of P, or that the erosion-reducing abatement actions that has been implemented has had an effect on the TP.

### 4.1.2 Agricultural stream (Støa)

Støa is a small stream on the Ra in the local western watershed draining into Western Vansjø (see Figure 4-1). The Støa stream originates from drainage pipes in an agricultural area, and represents thus a purely agricultural catchment. Opland (2011) found the drainage pipes in the nearby Huggenes field to be an important flow path for the transport of P due to P- transport through macropores down through the soil profile, and this is probably also the case in Støa. The soil is rich in iron, which leads to a high vulnerability to P losses under reducing condition caused by water-logged soils. Local farmers informs that they need to flush the drainage pipes due to Fe precipitation, indicating that there are frequently reducing conditions in the area.

The pH in the stream is circumneutral (Parekh, 2012). The Støa stream is rich in P. From 2004 to 2013 the (not volume weighted) year average TP concentration varied between 5.0 and 15.5 µM, with most years below 9.0 µM (Skarbøvik et al., 2014). Parekh (2012) found the median TP to be 3.5 µM, of which 52% was PP, 42 % DRP and about 6 % DUP. Transport of P with particles is thus important. The great amount of free DRP is caused by the fertilizers used in the area. TSS in Støa has been measured to be about 25 mg/L by high discharge and 5 mg/L at low discharge (Gebreslasse, 2012).

Water chemistry in Støa is dominated by base cations with 2.0 meq/L $Ca^{2+}$ and 0.6 meq/L $Mg^{2+}$ (Parekh, 2012).

### 4.1.3 Forest stream (Dalen)

Dalen is a small forest stream draining an area with only forest and peats, and it disembogues into Western Vansjø (see Figure 4-1). It has a low TSS, as erosion in areas covered with vegetation is low. TSS in Dalen has been measured to be about 4 mg/L by high discharge and 1 mg/L by low discharge (Gebreslasse, 2012). pH in the stream is around 4.5 (Parekh, 2012; Weldehawaria, 2013).

Ionic strength in Dalen is low (Parekh, 2012), while Al concentrations are high and monomeric Al (Ala, see Chapter 4.3.1.5 for definitions) has been measured to 20 µM (Weldehawaria, 2013) and 17 µM (Mohr, 2010), and in both cases about one quarter was inorganic monomeric Al (Ali). As discussed in Chapter 3.3.3, there has been a 67 % decrease in labile Al concentrations in South-Eastern Norway the last 30 years. There has probably also been a decrease in Dalen, and Al concentrations were probably substantially higher. This will

have affected the organic matter that was leached from the catchment, which has likely increased the last decades. DOC concentrations are quite high – as expected in forested catchments – and have been found to be 22 mg/L (Parekh, 2012) and 33 mg/L (Weldehawaria, 2013) by different studies.

The TP concentrations in Dalen are low and P is mostly associated with DOM. Since 2005 all year TP averages has remained below 0.8 µM (Skarbøvik et al., 2014). Weldehawaria (2013) and Parekh (2012) both found DTP concentrations of 0.2 µM, of which about three quarters were DUP and the remaining DRP.

### 4.1.4 Lake (Vansjø – Oksenøya)

The samples for the Lake were taken in Storefjorden, by Oksenøya (see Figure 4-1). In Vansjø, a neutral to slightly basic pH is measured (Skarbøvik et al., 2011). When there is low photosynthesis in Vansjø, the pH is normally around 7, while during summer the pH often increases due to the biological activity (Skarbøvik et al., 2011). During algal blooms, the pH can rise up to 10, and this pH change can further enhance the desorption of P (as discussed in Chapter 3.2.2) from particles leading to more P being available for algae and thereby increasing the problem.

TP concentrations in Storefjorden are normally higher in autumn and spring(1-2 µM) and decreases over summer to levels of 0.4 – 0.8 µM (Skarbøvik et al., 2014). Particle bound phosphorus (PP) is higher in periods of high discharge, like spring melt and autumn storms. PP varies mostly between 0.3 and 0.5 µM but lower and higher values are measured. DRP is normally around 0.2 µM in the summer, when the concentration is kept low due to grazing by algae, and 0.3-1.0 in autumn and spring. The TP and DRP concentrations will increase in the autumn due to autumn storms and turnover in the lake. This increase is normally seen in September-October (Skarbøvik et al., 2014).

TP concentrations in Vansjø are much lower than what would be expected from the amounts of P transported into Vansjø (Parekh, 2012). Massive amounts of PP is fed to the lake by Hobøl River, but little of this is found in the Lake, and actually the amounts of dissolved P that reaches the Lake would be enough to explain the TP concentrations. Thus, it is possible that PP simply sediments and contributes little to the total P levels.

## 4.2 Sampling and sample treatment

### 4.2.1 Sampling in streams

Samples were taken from agricultural (Støa), watershed (Hobøl) and forest (Dalen) streams during high discharge following a heavy rainfall in the morning 18th April 2013. Figure 4-2 below shows the discharge in the nearby Guthus stream in the time around the sampling. Sampling by high discharge was desirable as a great amount of P is transported during high flow, and Al concentrations in forested streams are expected to be higher.

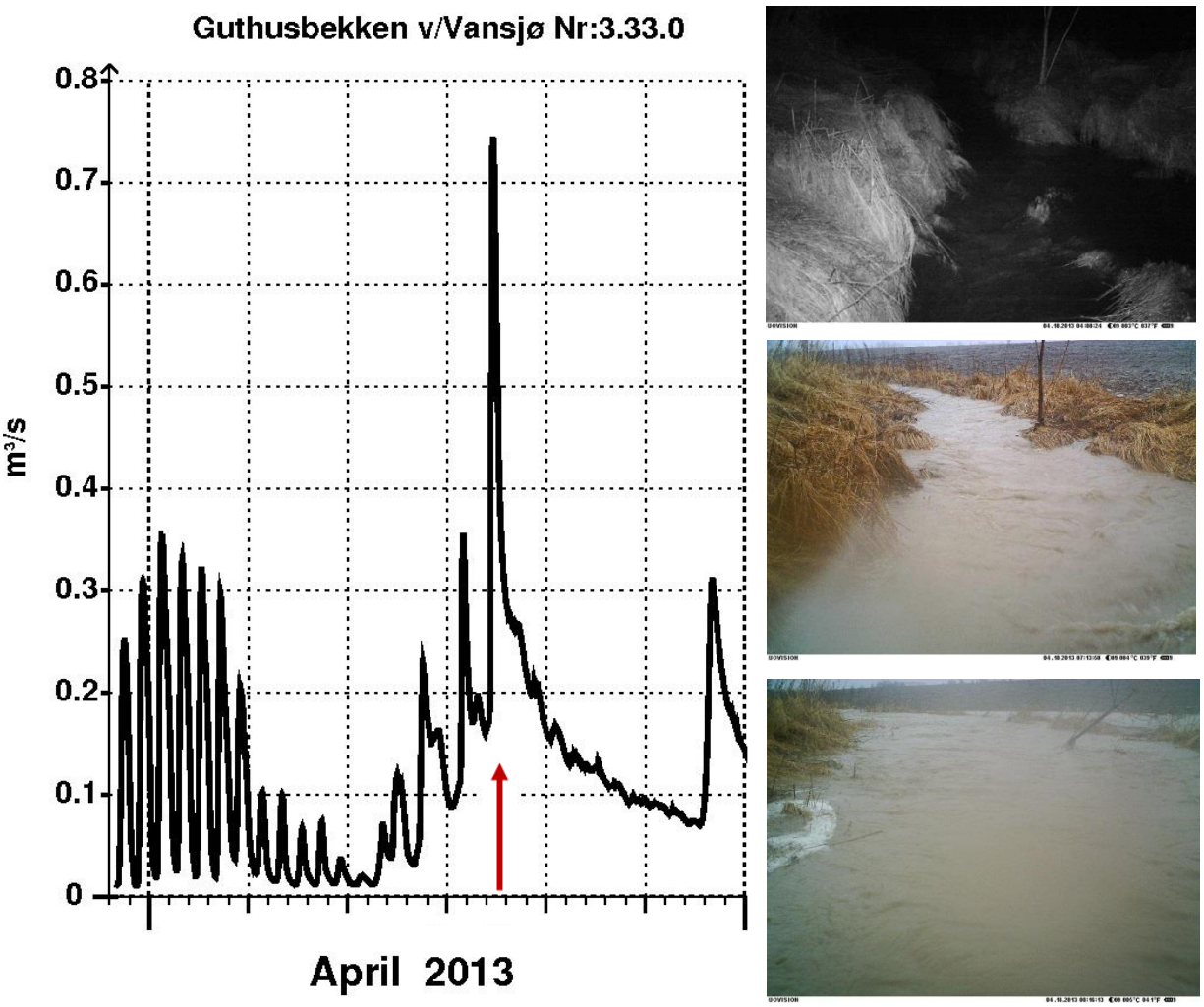


*Figure 4-2: Left: Water discharge in the Guthus stream around the time of sampling. The red arrow indicates the sampling day. Modified from Norges vassdrags- og energidirektorat (2013). Right: Pictures from the nearby Skuterud stream taken at 04:08, 07:13 and 08:16 on the morning of sampling. Photo: Marianne Bechmann.*

It is important to collect particles that represent the transported particles, and not the soil in the sampling point. Simply collecting stream water and use the suspended particles in the water would not give enough particles for characterization. To avoid digging into the stream

bottom and risk including soil, and at the same time collect enough particles for experiments and characterizations, a bilge pump connected to a sprinkler head was used to vacuum pump particles and water (see Figure 4-3). Two cans of 25 L were collected.

#### 4.2.1.1 Watershed stream

Figure 4-3 illustrates the high water flow at the time of sampling for the watershed samples (Hobøl), as well as the sampling equipment.

*Figure 4-3: The equipment used for sampling water and particles for experiments. Note the high water level during sampling of the Hobøl (left) and Støa sample (right). Photo: Rolf D. Vogt.*

#### 4.2.1.2 Agricultural stream

When sampling in the agricultural stream (Støa) the water flow was very high, with overland flow on fields and very high water flow in the small stream (Figure 4-3 and Figure 4-4). Thus, the sample is a mix of overland flow and water from drainage pipes. High water flow gives enhanced transport of particles, and the flooded fields may have given rise to reducing conditions. Previous studies refer to the sampling place as Støa1 (Gebreslasse, 2012; Parekh, 2012; Weldehawaria, 2013).

*Figure 4-4: Overflow water from the fields at Støa (left) and flooded stream in Dalen (right) on the day of sampling. Photo: Rolf D. Vogt.*

#### 4.2.1.3 Forest stream

Figure 4-4 illustrates the high water flow at the time of sampling in the forested stream (Dalen). The stream bottom was covered with ice, making sampling of streambed sediments impossible. However, the particle transport in the forest stream is normally low (Gebreslasse, 2012; Skarbøvik et al., 2014). The soils were less permeable for water as they likely were still partly frozen. Thus, rapid overland flow was the major flow-path, allowing for little or no time for equilibration with soil. This, coupled with the large precipitation event and contribution from melt water, will have affected the water quality. pH have been found to decrease and concentrations of inorganic monomeric aluminium (Alif) to increase during high discharge events (Seip, Andersen, Christophersen, Sullivan, & Vogt, 1989). This was however not seen in the characterization of the sample (see Chapter 5.1).

Most of the snow was gone in the watershed, as can be seen at the place of sampling on Figure 4-4.

### 4.2.2 Sampling in the lake

Water samples (5 cans of 25 L) were collected from the Lake Vansjø at Oksenøya, Storefjorden, in the evening 13$^{th}$ September 2013. During summer, DRP concentrations are low in Vansjø. Fall turnover causes concentrations of TP and DRP in the lake to increase, and occurs in September or October. The low TP concentration measured in the sample indicates sampling was done before fall turnover.

### 4.2.3 Sample handling and storage

#### 4.2.3.1 Storage and separation of water and particles

Water and particles were stored dark at 4° C. The water samples containing particles were left to settle for more than a month to ensure that most of the colloidal particles had sedimented. The particles were subsequently separated from the water by sucking the water up with a peristaltic pump. The particles from the two large containers were merged into a smaller flask. The water from the two 25 L cans were mixed to ensure homogeneous sample, giving the same starting point for experiments. The water was not filtrated, leaving some colloidal particles in suspension. This was in order to avoid unnecessary changes of the water samples, and as these smallest particles can act as flocculation nuclei for the precipitation reactions in the water-mixing experiment.

Precipitation of iron oxy-hydroxides in the samples from Støa was observed. This was later also observed in the particle container. The soils at Støa are rich in iron (Opland, 2011) and the prolonged wet snowmelt period had apparently given rise to reducing conditions in the flooded soils, allowing Fe(II) to be washed out of the soils.

#### 4.2.3.2 Sodium azide addition to particles

##### 4.2.3.2.1 Selection of preservation method

Biological activity and concomitant uptake of phosphate during storage or experiments are unwanted. Several conservation methods were considered, and addition of sodium azide to both water and particles was chosen as the preferred method. The main reason for using a chemical inhibitor was that it continues to inhibit biological activity over time. Thus, if bacteria are introduced later, the sample remains protected. This is an advantage when the samples are used for many experiments over a long time. The main disadvantages of sodium azide includes change of ionic strength (see Chapter 4.2.3.2.2) and change of pH (see Chapter 5.1.1), as well as toxicity also for humans. The latter is related to the formation of toxic gas (hydrazoic acid) when strong acid is added, necessitating work in ventilation hood.

Drying of the particles was considered as conservation method since there is insignificant biological activity in dry soils (Ellis & Stanford, 1988). Furthermore, dry particles are easier to handle, but the physiochemical properties of the particles will change (Ekholm, 1994; Olsen, 1958; Twinch, 1987). This is mainly due to that the smallest particles, that are very

important for sorption properties, will probably aggregate upon drying. Olsen (1958) reported that net adsorption of phosphate to dried sediments were clearly lower than for sediments that were kept wet, and excludes the possibility of making conclusions for natural sediments from experiments with dried sediment material. The standard materials kaolinite and illite which were used for the sorption-desorption experiments, were however procured as dried material.

Autoclaving is a widely used method for sterilizing soil samples, but leads to changes of the soil quality (Trevors, 1996). Furthermore, as the water samples sums up to a total of 275 L, autoclavation would be an unpractical procedure.

#### 4.2.3.2.2 Addition

The samples were left to equilibrate and stabilize in order to achieve a non-labile condition necessary for the experiments to be reproducible. The samples were therefore left for 2-4 months prior to adding sodium azide.

Adding 0.02 % (w/v) sodium azide to water, as done in several previous studies (de Vicente, Guerrero, Jiménez-Gómez, & Cruz-Pizarro, 2010; Liu, Liu, Tang, & Su, 2001; Łukawska-Matuszewska et al., 2013; Newell, Lucas, & Linley, 1981), caused an unacceptable increase in the conductivity of the watershed sample from 80 to 330 µS/cm. Thus, the added amount of sodium azide was reduced to 0.002 % (w/v), as conducted by Koelmans and Prevo (2003). 0.002 % (w/v) sodium azide was also added to the particle sludge (agricultural and watershed samples).

## 4.3 Analysis methods

Prior to addition of sodium azide, aliquots of water and particles were taken of the samples for characterization analyses that would be affected by the addition.

Deionized water with a resistance higher than 1 MΩ cm was used for all analyses, except for ion chromatography and ICP-MS measurements where water of 18 MΩ cm was used. Blanks of deionized water, going through the same sample preparation as the samples, were included for all analyses and experiments.

If nothing else is stated, laboratory work has been performed in laboratories at the Department of Chemistry, UiO.

### 4.3.1 Water analysis

The water samples were characterized in order to link observations in the experiments with the effect of the physiochemical matrix of the different water samples, as this governs the speciation and thus fractionation and precipitation of aluminium and phosphorous. Different filters were used for the filtration of the water samples for the different analyses, and this is indicated together with all the characterization results in Appendix, Paragraph 8.

#### 4.3.1.1 pH and conductivity

Conductivity and pH were measured on unfiltered samples according to ISO 7888 (1985) and ISO 10523 (2008), respectively. Conductivity was measured on a Mettler Toledo AG, FiveGo conductivity meter, calibrated using 84 μS/cm calibration solutions. pH in the collected samples and during the sorption-desorption experiment was measured using an Orion pH-meter with a ROSS pH electrode, while pH during the water-mixing experiment was measured using a Metrohm 744 pH meter with a Metrohm pH electrode and automatic correction of temperature. The pH electrodes were calibrated using buffer solutions at pH 4.00 and 7.00. For the characterization of the collected samples, conductivity and pH were measured on the day of sampling, as well as before and after addition of sodium azide. For experiments, pH and conductivity were measured before the experiment started and immediately after taking out an aliquot.

#### 4.3.1.2 Alkalinity

Alkalinity was measured potentiometrically in samples with pH greater than 5.5 by titration with 0.021 M acid to pH 4.5 according to ISO 9963-1 (1995), using an Ω Metrohm Swissmade 702 SM Titrino with a Metrohm 6.0262.100 Ecotrode Plus electrode. The alkalinity measurements are used for the calculation of bicarbonate concentration. This is done by subtracting the amount of acid equivalents needed to change the sample pH down to pH 4.5 and by calculating the buffering capacity by organic anions using the model by Oliver, Thurman, and Malcolm (1983). The buffering by other weak acids were assumed insignificant.

Alkalinity was measured before addition of sodium azide.

#### 4.3.1.3 Total suspended solids

Total suspended solids were measured according to ISO 11923 (1997) on samples added sodium azide.

#### 4.3.1.3.1 Selection of filter paper for experiments

The filter to be used should optimally have 0.45 µm pore size, as the common operational definition of particles is what does not pass through a 0.45 µm filter paper. Furthermore, the filter should not desorb any compounds interfering with the analysis or sorb any dissolved analytes, and the filtering should not take more than a few minutes. There have been several challenges in finding the right filter paper, and the result is that different experiments and analyses have been performed with different filter material and pore size (see Table 4-1). For details, see Appendix 8.7.

TSS was measured with three different filter papers to see if there was any difference in what the filters retained: 0.7 µm GF/F Glass Microfibre filter from Whatman (Cat. No 1825-047), 0.45 µm HAWP MF-Millipore Membrane (Cat. No. HAWP04700 and 0.45 µm Supor® polyethersulfone membrane filters from Pall. No significant differences were found. However, other investigations have shown significant differences (see Appendix 8.7), and it is concluded that the use of different filters can have significantly affected the results.

*Table 4-1: Overview of the filter papers that have been used, what they were used for, and problems that were encountered.*

| Filter | Pore size (µm) | Experiment | Problem |
|---|---|---|---|
| Cellulose Nitrate (CN) | 0.45 | Sorption-desorption<br>Characterization | Contamination |
| Cellulose Acetate (CA) | 0.45 | Sorption-desorption (filter comparison) | |
| Glass Fibre (GF) | 0.7 | Sorption-desorption (filter comparison)<br>Water-mixing | Pore size |
| MF Millipore (M) | 0.45 | Water mixing<br>Characterization | |
| Supor® Polyethersulfone (S) | 0.45 | Characterization | Slow filtration |

*CN: Cellulose Nitrate 0.45 µm filter from Sartorius (Cat. no. 13906 47 ACN)*
*AC: Cellulose Acetate 0.45 µm filter from Sartorius (Cat. no. 11106 47 ACN)*
*GF: GF/F Glass Microfibre 0.7 µm filters from Whatman (Cat. No 1825-047)*
*S: Supor®-450 Polyethersulfone 0.45 µm membrane filter from Pall (P/N 60173)*
*M: HAWP MF-Millipore 0.45 µm membrane filter (Cat. No. HAWP04700)*

#### 4.3.1.4 Phosphorus determination and fractionation

For measurements of phosphorus in solution the ISO 6878 (2004) method was followed; hereon referred to as the molybdenum blue method (MBM). This method is based on a reaction of orthophosphate ions with an acid solution containing molybdate and antimony ions to form an antimony phosphomolybdate complex. The complex is reduced with ascorbic acid to form a strongly coloured molybdenum blue complex, which is measured spectrometric at 880 nm to determine the concentration of orthophosphate. UV-1201 UV-Vis Shimadzu spectrometer and UV-1800 UV-Vis Shimadzu spectrometer were used for the determination of orthophosphate concentrations. Limit of detection (3 times the standard deviation of 10 blanks) was measured to be 0.08 µM P, and the limit of quantification (10 times the standard deviation of 10 blanks) was 0.26 µg P/L.

The dissolved P fractions are determined after filtration of the sample through 0.45µm membrane filter and 0.7 µm glass fibre filter for comparison. For measurements of the total P content, the sample is oxidized with potassium peroxodisulphate in an autoclave for 30 minutes prior to measurements. Based on different sample pre-treatment regarding filtering and digestion the P was fractionated into total phosphorus (TP), dissolved total phosphorus (DTP), particulate phosphorus (PP), dissolved reactive phosphorus (DRP) and dissolved unreactive phosphorus (DUP) as illustrated in Figure 4-5. PP and DUP is found by the difference between TP and DTP, and DTP and DRP respectively. DUP includes the P bound in dissolved organic matter (DOM).

For the MBM method, a relative reproducibility between laboratories of about 10 % is reported both for orthophosphate and digested samples (ISO 6878, 2004). However, an inter-laboratory comparison in Norway showed low accuracy and poor precision for TP within and between laboratories (Krogstad, Øgaard, & Skarbøvik, 2013). Non-representative sample outtake of aliquots containing particles was considered the most probable explanation. Sample outtake was also found to be a problem in the current sorption-desorption experiment (see Chapter 5.3.1).

To ensure accuracy of the P measurements, an independent P control standard, made by a another qualified person using a different phosphate salt, was measured alongside the standards. As a quality control of the decomposition and measurements of TP, the solutions with known concentrations from the investigations of Krogstad et al. (2013) – mentioned above – were analysed alongside the samples.

The definition of the dissolved fraction is simply what passes through a 0.45 µm membrane. However, different types of 0.45 µm filter papers can give different results. This is speculated to be due to different degree of sorption to different materials as well as that the sorption can be affected by the filtration time (which should not exceed 10 min). The different filters materials differ in properties such as hydrophobicity, which affect the degree of sorption and rate of filtration.

P fractionation was determined after addition of sodium azide.

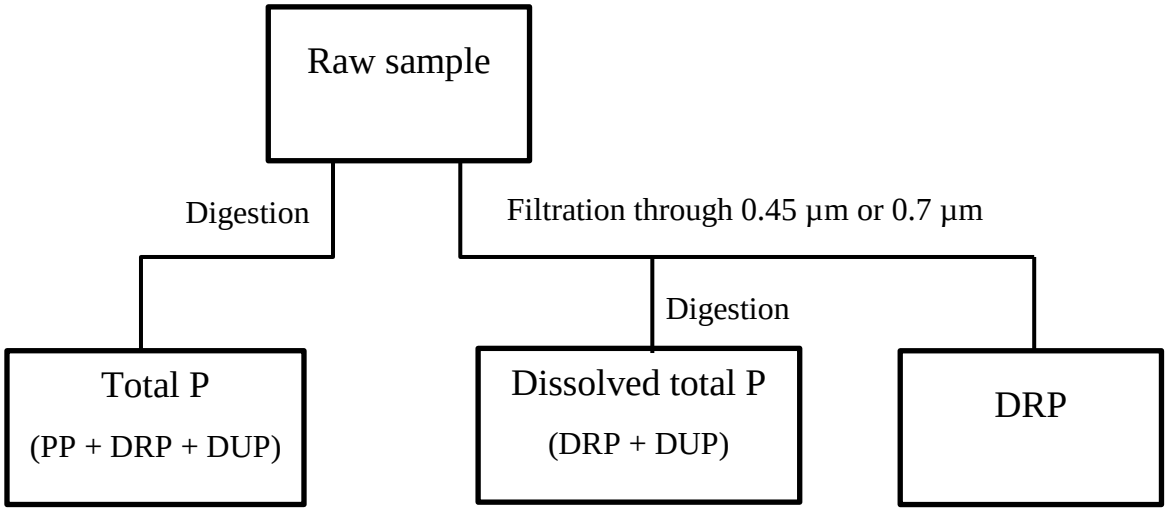


*Figure 4-5: Phosphorus fractionation scheme for the molybdenum blue method (MBM).*

#### 4.3.1.4.1 Deviations from Phosphorous ISO method

After adding colour-developing reagents, the ISO standard method (ISO 6878, 2004) states that the sample should be diluted to 50 mL in order to get the same total volume for all samples and standards. This was not done, as many samples were close to detection limit, and dilution would lead to poorer detection. Instead, the same amounts of reagents were added to the same volume of sample and calibration standards, giving the same total volume.

For the sorption-desorption experiments and two of the water-mixing experiments, the procedures for measuring DRP were modified by addition of 0.04 M sulphuric acid to the samples and the standards for preservation. This was in accordance with the former Norwegian standard method for determination of phosphate (NS4724, 1984). Acidification of DRP samples will however change the equilibrium between non-reactive (mainly organic) and reactive inorganic bound phosphate, thereby increasing the apparent DRP in expense of DUP. As a response to unexpected results in the water-mixing experiment, acidification of the

DRP samples was abandoned to see if this affected the results. However, the expected results were still not seen.

#### 4.3.1.4.2 Testing the MBM method

Different tests were performed to check the robustness of the molybdenum blue method (MBM). The blue colour that is used to determine the P concentration was found to be stable after 8 minutes, and after that the measured concentration changed only 0.06 µM within the first 4 hours (see Appendix Chapter 8.10.1).

##### *4.3.1.4.2.1 Effect of pH*

After the digestion of TP and DTP samples, the samples should according to the MBM method be adjusted to have a pH between 3 and 10. Due to trouble experienced by colleagues with this pH adjustment, a check of the effect of pH on the colour development was performed.

0.3 and 4.8 µM P calibration standards were added different amounts of sulphuric acid (from 0.036 M to 0.436 M). The lowest amount of added acid corresponds to what is used in the MBM method for the conservation of samples for TP and DTP measurements. As the test was performed on pre-acidified standards, there are no data for standard without acid. There is a strong effect of pH on the colour development (Figure 4-6).

The test shows that the pH adjustment of acidified samples is necessary. Additionally, this is another reason for not acidifying the DRP samples as discussed above, as it can alter the colours development in addition to the fractionation between DRP and DUP.

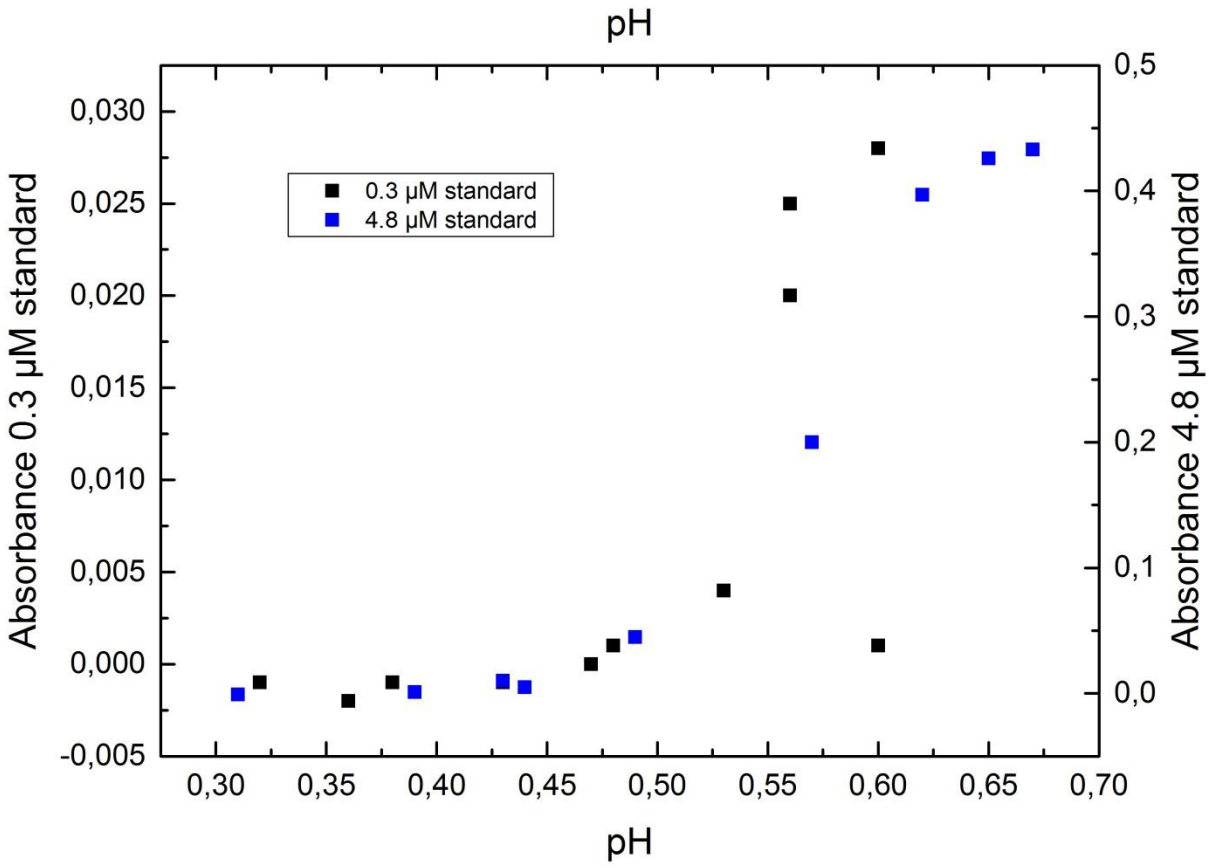


*Figure 4-6: Absorbance measured with the MBM method as a function of the pH after addition of sulphuric acid to the 0.3 and 4.8 µM P standards.*

#### *4.3.1.4.2.2 Check of complete digestion*

To check if digestion was complete after doing the digestion procedure once, duplicates of samples from the three streams were made for determination of total and dissolved total phosphorus (TP and DTP), and the first sample was digested once and the second twice, adding potassium peroxodisulphate also before the second round. The variation in P concentration after one and two digestions seem random, thus the samples seem to be completely digested after 30 min in the autoclave.

Others have reported 400 mg/L of suspended solids as an upper limit for use of the MBM method (Krogstad et al., 2013). This is four times more than what was used in the sorption-desorption experiments, and supports that the digestion should be complete.

*Table 4-2: Results from comparison of one and two digestions of samples for TP and DTP analysis. This was done to check that the digestion was complete after one digestion.*

| | Concentration (µM) | |
|---|---|---|
| | **One digestion** | **Two digestions** |
| TP | | |
| Agricultural (Støa) | 5.7 | 5.5 |
| Watershed (Hobøl) | 2.6 | 2.6 |
| Forest (Dalen) | 0.1 | 0.2 |
| DTP | | |
| Agricultural (Støa) | 3.0 | 2.9 |
| Watershed (Hobøl) | 2.1 | 1.9 |
| Forest (Dalen) | 0.1 | 0.1 |

#### 4.3.1.5 Aluminium determination and fractionation

Concentrations of aluminium fractions were measured according to the methods of Barnes (1975) and Driscoll (1984) in the water-mixing experiment. Monomeric Al is complexed with 8-hydroxyquinoline and extracted into methyl isobutyl ketone before spectrometric measurement (Barnes, 1975). The mixture is shaken for 20 seconds, allowing only dissolved and readily reactive (labile) species of Al to be determined.

Different Al fractions were determined by a combination of different sample pre-treatment using 0.45µm filtration, cation exchange and acid digestion prior to determination of the Aluminium concentration according to the method by Barnes (1975). Aqueous aluminium was fractionated into acid reactive aluminium (Alr), acid reactive aluminium in filtered sample (Alrf), monomeric aluminium (Ala), monomeric aluminium in filtered sample (Alaf), non-labile monomeric aluminium in filtered sample (Alof) and labile monomeric aluminium in filtered sample (Alif). Measurements were performed on filtered samples as it was conceivable that some of the freshly formed particles in the water-mixing experiment could be labile enough to dissolve and be detected by the Barnes (1975) method. Using not filtered samples could thus lead to some particulate Al being measured as Ala, introducing uncertainties in the interpretation of the results. In the second Low P Concentration experiment, where both Ala and Alaf were measured, the Ala was significantly higher than the Alaf ($p < 0.0001$ on a paired t-test) but the same pattern was seen for the two fractions. This indicates that it would make no difference to perform these measurements on non-filtrated samples as we are interested in the trends.

The acid reactive aluminium (Alr and Alrf) was measured minimum 1 h after digestion by acidification to pH 1, transforming colloidal aluminium, polymeric aluminium and very strongly bound alumina-organic forms of aluminium to monomeric aluminium (Driscoll, 1984).The Alif is the difference between Alaf and Alof.

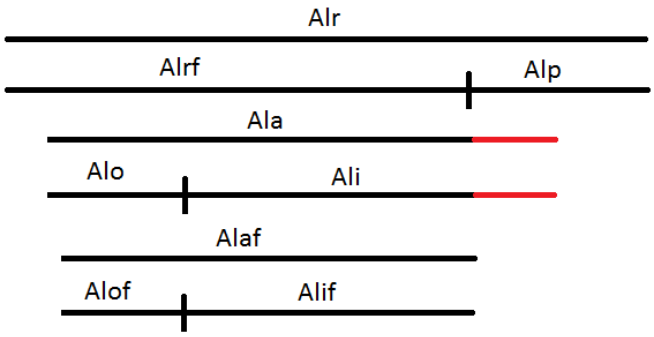


*Figure 4-7: Al fractionation scheme illustrating that some of the particulate P may be measured as Ala without filtration. Alp refers to the particulate fraction of Al; the difference between Alr and Alrf.*

The non-labile monomeric aluminium (Alof) is mainly organically complexed monomeric aluminium in the filtered sample (Driscoll, 1984), making the labile monomeric aluminium (Alif) a measure of the inorganic monomeric aluminium in the filtered sample. Alif includes aquo aluminium as well as hydroxide, sulphate and fluoride complexes of monomeric aluminium. To separate the non-labile (Alof) and labile monomeric aluminium (Alif) the sample is passed through a pH adjusted cation exchange column (Amberlite IR-120). The Ali is positively charged and stays on the column, while the neutral or negatively charged Alo passes through. Above pH 5.5 $Al(OH)_4^-$ begins to form in significant amounts, and the fractionation of Ali and Alo by charge is no longer applicable. As the pH of the water-mixing experiment mainly varied between 6.0 and 7.3, the Alif and Alof results must be interpreted with care. For the last experiments it was instead decided to measure only Alr, Alrf, Ala and Alaf, and drop the Alo determination.

UV-1201 UV-Vis Shimadzu spectrometer and UV-1800 UV-Vis Shimadzu spectrometer were used for analyses. Samples were measured by λ 395 nm and absorbance at 600 nm, is used for Fe correction. Aluminium fractionation was measured after addition of sodium azide.

To validate the accuracy of the method, the Al stock solution was measured with ICP-OES calibrated by a set of standards prepared using a commercial stock solution.

#### 4.3.1.6 Natural organic matter

Absorbance at λ 254, 400 and 600 nm was measured on the samples to get a proxy for the amount and quality of organic matter in the water samples. UV-1201 UV-Vis Shimadzu spectrometer and UV-1800 UV-Vis Shimadzu spectrometer were used for the analyses with a 10 mm quartz cuvette. Measurement on non-filtrated sample gives information about total natural organic matter (TNOM) and measuring on filtrated sample about dissolved natural organic matter (DNOM). The difference between the two is the particulate natural organic matter (PNOM).

The absorbance at 254 nm is generally found to be positively correlated with the total organic carbon (TOC) in the sample (Dobbs, Wise, & Dean, 1972) since the aromaticity is rather evenly distributed in the NOM, giving a rather constant sUVa.

The specific UV absorbance (sUVa) – the absorbance of a water sample at 254 nm divided by the dissolved organic carbon (DOC, in mg C/L) content – is a measure of the aromaticity of the organic matter in the water sample (Weishaar et al., 2003). The specific absorbance ratio (SAR) between the absorbency at 254 nm and 400 nm decreases as the molecular weight of aquatic humic solutes increases (Hautala, Peuravuori, & Pihlaja, 2000; Peuravuori & Pihlaja, 1997).

UV/Vis absorption was measured on sample added sodium azide.

#### 4.3.1.7 Dissolved organic carbon

Dissolved organic carbon (DOC) was measured on samples filtered through 0.45 µm filter paper, as the instrument can be damaged if particles enter the instrument. It was measured following an automated pre-treatment by acidification and purging of the sample with a carbon free gas to remove inorganic carbon (i.e. bicarbonate) as $CO_2$. Volatile substances can thus escape, but the DNOM we are interested in is non-volatile. The organic carbon is oxidized to $CO_2$, by catalytic high temperature combustion, which is measured in the IR range (ISO 8245, 1999).

Measurements were performed on a TOC-V CPH instrument from Shimadzu at the Department of Biology, University of Oslo, by colleagues Christian Wilhelm Mohr and Andreas Lislerud Smebye at Department of Chemistry. Samples were not added sodium azide.

#### 4.3.1.8 Major anions and cations with ion chromatography

Analysis of major anions ($F^-$, $Cl^-$, $Br^-$, $NO_3^-$ and $SO_4^{2-}$) concentrations was performed on 0.45 µm filtered samples on a Dionex ICS-2000 Ion Chromatography System (ICS-2000) at the Department of Geosciences, University of Oslo, following Standard Methods for the Examination of Water and Wastewater, Method 4110B, Standard Methods (1992). The instrument performs ion analyses using ion supression. Anions are separated according to their affinity for a low capacity-strongly basic anion exchange resin.

Analysis of major cations ($Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) concentrations was performed on the same instrument as the anions following a similar method, with an electrolytically generated methanesulphonic acid as eluent instead of KOH and a cation exchange column for separation.

For calculations of the ion balance, the organic charge was estimated from pH and DOC by the method of Oliver et al. (1983).

Anions and cations were measured on sample not added sodium azide. For operating conditions for the anion and cation determination, see Appendix 8.11.1and 8.11.2.

#### 4.3.1.9 Major cations by ICP-OES

Major cation determination were also conducted on 0.45 µm filtered water samples using a Varian (Australia) Vista AX CCD simultaneous axial view inductively coupled plasma optical emission spectrometry (ICP-OES) equipped with V-groove nebulizer with Sturman-Masters spray chamber. The analysis was performed by colleague Christian Wilhelm Mohr at Department of Chemistry according to the manual of the instrument. For operating conditions see Appendix, Paragraph 8.11.3.

Cations were measured on sample not added sodium azide.

#### 4.3.1.10 Trace metals by ICP-MS

Concentrations of dissolved trace metals (Fe, Al, Cr, Mn, Cu, Zn, As, Cd, Sn and Pb) where measured on 0.45 µm filtered samples using a NexION® 300X inductively coupled plasma mass spectrometer (ICP-MS) from PerkinElmer. The analysis was performed by colleague Tina Bryntesen (experienced with ICP-MS) at the Department of Chemistry, University of Oslo, with standards made by Christian Wilhelm Mohr (same affiliation). For wavelengths used see Appendix, Paragraph 8.11.4.

Trace metal analysis was performed on sample not added sodium azide.

### 4.3.2 Particle analysis

All particle analyses were performed on samples not added sodium azide.

#### 4.3.2.1 Organic content by loss on ignition

Pre-dried samples were burned at 550° C for three hours, and the difference in weight was used to estimate the organic content.

#### 4.3.2.2 Phosphorus content

Phosphorus in the particles was fractionated into organically and inorganically bound by the method of Møberg and Petersen (1982). Inorganic phosphorus is extracted by using 6 M sulphuric acid and heating the sample to 70° C. Total phosphorus is extracted in the same way from a sample that has been burned by 550° C, and the difference between the two fractions is an estimate of the organic fraction.

#### 4.3.2.3 Mineralogy

To analyse the mineral content of the particles, X-ray diffraction (XRD) (insert instrument details) was performed. The computer program TOPAS version 4-2 was used to interpret the signals.

#### 4.3.2.4 Particle size distribution

To determine particle texture of the particle samples, particle size distribution (PSD) was analysed with a Beckman Coulter LS 13 320 laser diffraction particle size analyser. Samples were freeze dried and set in an ultrasonic bath with 5 % sodium metaphosphate for complete dispersion of the particles prior to analysis. This method has been compared with the ISO 11277 (2009) and the small differences in the results were found to be satisfying for the use in this master thesis (Pettersen, 2014).

Analysis was performed by colleague Ellen Pettersen at Department of Chemistry, University of Oslo.

The results were categorized as clay(< 2 µm), silt (2 - 63 µm) and sand (63 µm – 2 mm), and the particle texture is determined as described in vanLoon and Duffy (2011).

## 4.4 Use of radioactive phosphorus in the water-mixing experiments

The P concentrations in natural waters are often close to the detection limit for analytical methods like the MBM method and ICP-MS. To be able to detect lower concentrations and verify the results from the MBM method, a radioactive isotope of P ($^{32}$P) was added in the water-mixing experiments, and the P fractionation was measured by liquid scintillation counting (LSC) in addition to the MBM method. The activity of $^{32}$P was measured in the filtrate and on the filter residue, giving the dissolved (D$^{32}$P) and particulate (P$^{32}$P) fractions. A Hidex 300 SL automatic liquid scintillation counter was used for the measurements.

Quenching can cause interference in LSC (see Appendix, Chapter 8.6). The LSC instrument has a built-in function for quench correction called the triple to double coincidence ratio (TDCR). The TDCR method is reported to be accurate to 5 % (Southern Scientific Ltd, 2012), which is considered satisfactory for the purpose of these investigations. Testing of the TDCR method concluded that the method gives a sufficient accuracy (see Appendix, Chapter 8.6), and the quench corrected activity (disintegrations per minute, DPM) calculated by the instrument based on the TDCR value is used in the results.

To correct for adsorption of dissolved P to the filter paper, deionized water with $^{32}$P concentration similar to what was used in the experiments was filtered, and the filter paper was counted in LSC, as done by others e.g. Pierce (1982). See Appendix Paragraph 8.9 for results.

## 4.5 Experimental design

Two different types of experiments have been performed in order to investigate the role of particles and phosphorus bound to particles in eutrophication.

The first one was investigating the sorption of phosphorus to particles in water with high P concentration, and desorption from the particles when they enter water with lower P concentrations. Thus, the experiment consists of a sorption part and a desorption part.

The second experiment assessed the water quality change when water from agriculture is mixed with water from forest. Of special interest was formation of particles and phosphorus associated with these newly formed particles or particles already present. This experiment

also consisted of two parts: one mixing part and one part where desorption from the particles from the first part was investigated.

### 4.5.1 Sorption and desorption of phosphorus to particles

The main transport of phosphorus to Lake Vansjø is in association with particles (PP). Most of these particles stem from agricultural land, where erosion is high and the P content of the soil is elevated due to use of fertilizers. The DRP concentration in the agricultural streams is also often high, and particles can sorb more P from the water. When this PP reaches the lake, it is not necessarily available for biological uptake: It might stay bound to the particles and sediment. It can also be released to the water as DRP. As the DRP concentration in Vansjø is much lower than in the agricultural streams, the desorption of P can be favoured and contribute to the algal growth in Vansjø. The release can also happen after sedimentation, though high sedimentation rate might contribute to burying P rich particles and thus reduce the internal loading of P to the water column. Considering that many abatement actions in the Vansjø-Hobøl catchment focuses on reducing the erosion and transport of particles, to know the fate and impact of the PP is obviously important.

Four sorption-desorption experiments (

Table 4-3) were conducted with particles and water from the Watershed stream (Hobøl): 1) A blank experiment added no extra P, experiments added 2) low and 3) high concentration of P (as $Na_2HPO_4$), and 4) an experiment added low concentration of P but filtered with two different filter papers for comparison. Two distinctly different clay minerals illite and kaolinite are used as standard materials. Illite is a 2:1 clay while kaolinite is a non-swelling 1:1 clay. The kaolinite used is KGa-2 Kaolin, high-defect, Warren County, Georgia, USA from Clay Mineral Society. The Illite material is of unknown origin. Gebreslasse (2012) found 0.7 to 7.2 % illite, with an average of 2.9 % in stream sediments collected in the Vansjø-Hobøl catchment. Water used for the experiment is from the watershed river and Deionized water.

The particle concentration in the experiment was chosen to be 100 mg/L based on the TSS concentrations in the Watershed (Hobøl) river by high discharge.

The four experiments consist of two parts: sorption and desorption. During the sorption part, the particles were spiked with P by exposing the particles to water spiked with an appropriate concentration of $PO_4$ on a shaking table for 12 hours; thereafter the mix was left to rest overnight allowing the particles to sediment. The water was decanted, and the particles used for the desorption part of the experiment where water with low P concentration was added. The main focus of this study was on the desorption of $PO_4$ when P rich particles are washed into Lake Vansjø, were the $PO_4$ concentration is low. Thus, the desorption part of the experiment was monitored closely with time, while the sorption part was only sampled in the beginning and end to calculate the sorbed amount. The desorption part was monitored for 4 days.

P fractionation, pH and conductivity were measured over time during the experiments. Effort was made to take out aliquots with as representative water to particles ratio as possible in order to keep this ratio constant throughout the experiment. The same water was used for both for sorption and desorption parts of the experiment, but for the desorption part the phosphate in the watershed sample was first decreased by precipitation $Al^{3+}$ added as a solution of $KAl(SO_4) \cdot 12\ H_2O$.

*Table 4-3: Overview of the sorption-desorption experiments that were performed. All experiments were added 100 mg/L particles.*

| Experiment | Added P in sorption part (µM) | Added P in sorption part (µmol/g particles) | Total DRP in water before adding particles (µM) | Water for Desorption Part | Filter |
|---|---|---|---|---|---|
| Blank | 0.0 | 0.0 | 1.5 | Watershed + 21 µM Al | CN |
| Low conc. | 1.6 | 16 | 3.1 | Watershed + 21 µM Al | CN |
| High conc. | 3.2 | 32 | 4.8 | Watershed + 21 µM Al | CN |
| Filter comparison | 1.6 | 16 | 3.1 | Watershed + 48 µM Al | CA and GF |
| Kaolinite | 0.0 | 0.0 | 0.0 | Deionized water | CN |
| Illite | 0.0 | 0.0 | 0.0 | Deionized water | CN |

*Watershed = sample from Hobøl*
*GF: GF/F Glass Microfibre 0.7 µm Filters from Whatman (Cat. No 1825-047)*
*CN: Cellulose Nitrate 0.45 µm Filter from Sartorius (Cat. no. 13906 47 ACN)*
*AC: Cellulose Acetate 0.45 µm Filter from Sartorius (Cat. no. 11106 47 ACN)*

For the sorption-desorption experiments, DRP measurements were performed on filtrated water after acidification, which (as discussed in Chapter 4.3.1.4.1) is not according to the present ISO standard and might have shifted the equilibrium between DRP and DUP.

A filter comparison experiment was performed to investigate the difference between the use of 0.45 µm and 0.7 µm filter papers, thus two samples were taken out at each time interval and filtrated with the two different filter papers. In this experiment glass fibre filter paper was used for the 0.7 µm filtration and cellulose acetate (CA) filter paper was used for the 0.45 µm filtration. In all other experiments cellulose nitrate (CN) filter paper were used (see Chapter 4.3.1.3.1).

The filter comparison experiment was performed with the same amount of P in the sorption part as the Low concentration experiment (1.6 µM). Experience from the Blank, Low and High P concentration experiments made us use more Al in the preparation of the water for the

desorption part, to achieve a lower starting concentration of P. This was done in order to make the desorption of P easier to detect, but it makes the experiment difficult to compare with the other experiments as both the filter paper and the water quality are different.

### 4.5.2 Particles formed when water from forested and agricultural catchments are mixed

The aim was to investigate the fate of phosphate when acid and Alif rich water from a forested catchment (Dalen) mixes with circumneutral pH and phosphate rich water from an agricultural catchment (Støa). Particles are expected to form (Shekobe, 2012), but it is unclear what happens to the phosphate fractions in solution. Do they bind to the particles in the stream or in the lake and are they desorbed again upon entering the lake? Shekobe (2012) found that Al did form particles and that phosphate and organic material was sorbed to these particles.

Water draining from an agricultural catchment usually has close to neutral pH and often high concentrations of free phosphate. Water draining from an forested catchment with acid soils will have a low pH, and elevated concentrations of dissolved natural organic material (DNOM) and labile Al (Ali). When two such water qualities are mixed, particles are expected to form, as the aluminium hydrolyses to form $Al(OH)_3$ which has very low solubility at pH 6 – 8. This amorphous Al oxy-hydroxides (AlOOH) has a net positive charge (pH at pzc is around 8.2) and is therefore an effective sorption site for orthophosphate. This is thus a possible important removal process for phosphate in a catchment. During the acid rain period there were higher concentrations of Al in the water from the forest, implying that this precipitation was assumedly then a more important removal process for phosphate than it is today.

The experiment consists of two parts: Mixing (see Figure 4-8) and desorption (see Figure 4-9). First, equal volumes (2 L) of water from the agricultural and the forested catchment were mixed (Figure 4-8). The water from the agricultural catchment was spiked with radioactive and stable phosphate (as $Na_2HPO_4$), and the water from the forested catchment was either used untreated or spiked with aluminium to 26 µM $Al_a$ and pH was adjusted to 3.8 or 4.5 with sulphuric acid to simulate the acid rain period. For the experiments where there was no aluminium added, the pH was not adjusted.

If the pH of the solution is above 5.5 the method of Driscoll (1984) for fractionating Alo and Ali is not applicable. These fractionation data need thus to be interpreted with care (see Chapter 4.3.1.4.2).

The mixing part of the experiment was continued for 2 days, and the desorption part for 2-16 days. The fractionation of P and Al was monitored with time, as well as the UV/Vis absorbency, pH and conductivity. As a response to unexpected results (no observed particle formation) acidification of the samples for analysis of DRP were abandoned (see Chapter 4.3.1.4.1), filter papers were changed from 0.7 to 0.45 µm (see Chapter 4.3.1.3.1) and the measured Al fractions were changed from Alaf, Alof and Alr to Alaf, Ala, Alrf and Alr (see Chapter 4.3.1.4.2).

The highest added P concentration to the agricultural water was 4.8 µM. This value was chosen as the resulting DRP concentration in the sample after the addition (6.4 µM) was similar to previously measured high DRP concentrations in the agricultural stream (Parekh, 2012).

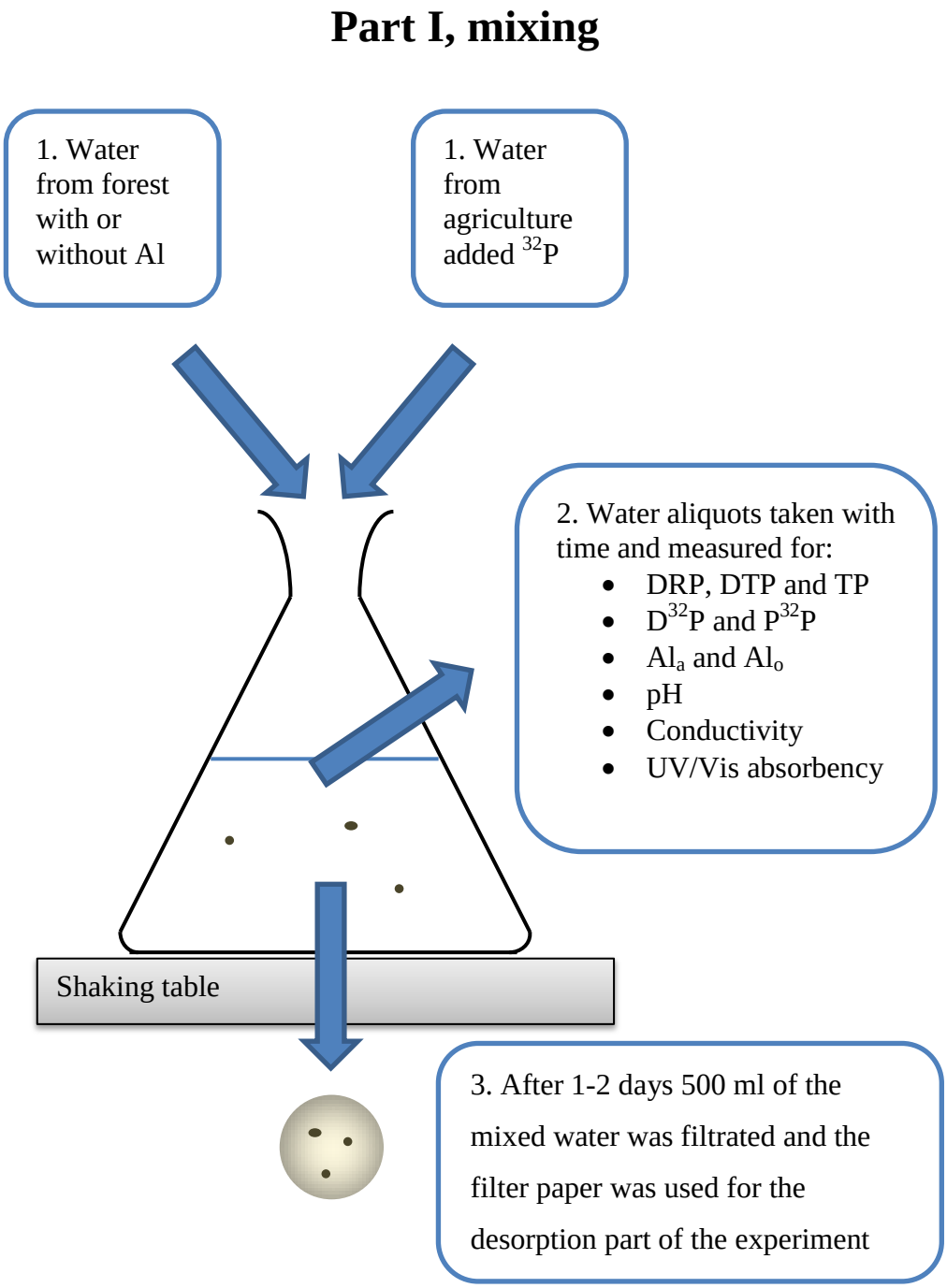


*Figure 4-8: Part I of mixing experiment. Water was mixed, and sample aliquots were taken out with time to monitor fractions of P, Al and NOM, and pH and conductivity. The rest of the water was filtrated and the filter paper was used for part 2 of the experiment; desorption.*

After a given time, about 500 mL of the mixed sample was filtrated, and the filter paper with particles was used for desorption experiments (Figure 4-9): The filter paper was added to water from the lake, which contains low concentration of phosphate, and desorption of P fractions with time was measured together with pH, conductivity, UV/Vis absorbency and fractions of Al.

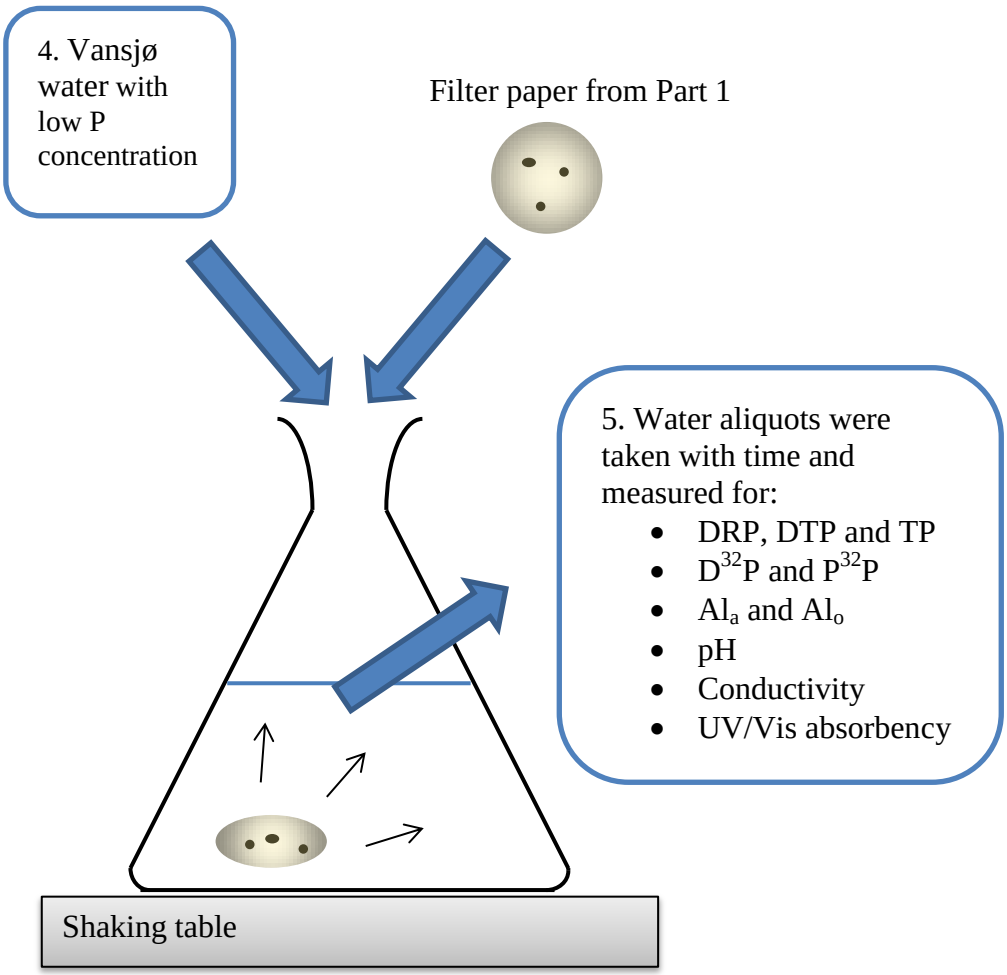


*Figure 4-9: Part II of the mixing experiment. The filter paper from the mixing part was added to water from Lake Vansjø, which had low concentrations of P. Desorption from the filter paper was monitored with time.*

#### 4.5.2.1 Overview of experiments

The water-mixing experiment was performed with varying Al and P concentrations (see Table 4-4). The low P concentration experiment was measured thoroughly with long time series and repeated to confirm results, while the blank and the high P concentration experiments were carried out with less subsamples as the results from these experiments will only be used for qualitative comparison.

Radioactive $^{32}P$ was added in the blank and low P concentration experiments. The amounts that are added are not measureable with the MBM method, thus the P concentration is practically the same as originally in the sample. The blank was a mix of the water from the forested catchment (Dalen), representing today's Al concentration, and water from the agricultural catchment (Støa). Aluminium was added to sample from the forested catchment used for the low and high P concentration experiments increasing the concentration by 17 µM Al to a total of 26 µM monomeric aluminium (Ala). This is meant to represent the higher levels during the past acid rain period. The high P concentration experiment was also added 4.8 µM P to the agricultural water sample, which is about twice as much as the original DTP concentration. In this experiment, the pH was lowered more than in the two Low P concentration experiments to see if the different pH levels would have any effect.

*Table 4-4: Overview of water-mixing experiments showing methods modifications for different experiments, and amount of P and Al that was added to the water samples collected in the agricultural and forested catchment, respectively.*

| Experiment | Forest water: Added Al | pH of forest water | Agricultural water: Added P | Filter | Acidification of DRP samples? | Measured molar ratio $Al_{af}$ :DRP |
|---|---|---|---|---|---|---|
| Blank | 0 µM | 5.6 | Only $^{32}P$ | Glass fibre 0.7 µm | Yes | 4.1 |
| Low P experiment I | 17 µM | 4.5 | Only $^{32}P$ | Millipore 0.45 µm | No | 9.6 |
| Low P experiment II | 17 µM | 4.5 | Only $^{32}P$ | Millipore 0.45 µm | No | 6.5 |
| High P experiment | 17 µM | 3.8 | 4.8 µM, no $^{32}P$ | Glass fibre 0.7 µm | Yes | 4.6 |

There were quite high variation in measured aluminium concentration (see Table 8-1 in Appendix, Paragraph 8), thus the molar ratios (that are based on measured values for each experiment) are not the same for the two low concentration experiments.

Due to unexpected results, type of filter paper and method used for measuring DRP was changed (see Chapter 4.3.1.4.1 Deviations from Phosphorous ISO method and 4.3.1.3.1 Selection of filter paper for experiments)

The conservative mix is the concentrations expected from mixing the two water qualities based on the characterization of the waters from the forested and agricultural stream. I.e. what would be measured if no chemical reactions occur upon mixing. It is calculated from the measurements from each experiment, and not from the characterization data that are the average of several measurements. This was chosen due to that the P and Al added before the experiment started distributed among the different fractions, and assuming that all of this was in the dissolved fraction would lead to erroneously high change from the conservative mix to the measured samples after mixing.

The data for Conservative mix are the concentration expected from mixing the two water qualities based on the characterization of the waters from the forested and agricultural stream. I.e. what would be measured if no chemical reactions had occurred upon mixing. The P and Al added prior to the experiment was distributed among the different fractions. These Conservative mix data are therefore calculated from the measurements of water chemistry before mixing from each experiment, and not from the characterization data presented in Chapter 5.1 that are the average of all the measurements.

As the TP measurements were more stable in this experiment than in the sorption-desorption experiment, the results have not been corrected to a constant TP.

## 4.6 Logarithmic regression

Linear regression on log-transformed time – from now on referred to as logarithmic regression – was used to investigate the trends during the sorption-desorption experiment and the water mixing experiment. Logarithmic regression was chosen as changes are expected to happen quickly in the beginning of each part of the experiment, and then slow down. The plot of the residuals was inspected to see if the regression is appropriate. The theoretical starting concentrations (the concentration in the conservative mix in the mixing part water-mixing experiment and the concentration in the water used for the desorption parts of both experiments) are not included in the regression as the time 0 is incompatible in logarithmic regression. As the possible biggest change happens from the start of the experiment to the first

sample, the exclusion of time 0 makes detection of changes and trends with the regression more difficult. Thus, a separate comparison with time 0 is made in the text to overcome this problem.

Consistent trends in an experiment is considered as having a trend with $|R| > 0.7$) in all experiments, in the same direction.

## 4.7 Modelling the effect of pH on sorption

Modelling is performed in PHREEQC to show how the sorption of phosphate changes with pH. PHREEQC version 3 is a computer program written in the C and C++ programming languages that is designed to perform a wide variety of aqueous geochemical calculations. The output from PHREEQC is imported to the computer software R to make the graphs that are displayed here. R is an integrated suite of software facilities for data manipulation, calculation and graphical display. Both PHREEQC and R are available on the Internet free of charge.

The modelling is performed for hydrous ferric oxide as iron is very important for P transport. Hydrous ferric oxides are a class of minerals that form from the weathering of minerals that contains hydroxides and iron. They can act as sorbents and are thus interesting to look at regarding phosphate in solution. They are highly porous, poorly crystalline and have large surface areas.

Equilibrium constants (K) decide the distribution of elements between solution and adsorption to surface. Log(K) values for the hydrous ferric oxide are defined in the llnl database of PHREEQC that is used in the simulations.

The particle concentration used in the modelling was the same as in the sorption-desorption experiment (0.1 g/L). The pH in the model was varied between 1 and 14. As the modelling were made to simulate the laboratory experiments, a water temperature of 25° C was used instead of the 0-20° C found in nature.

# 5 RESULTS AND DISCUSSION

## 5.1 Characteristics of water used in the experiments

In order to assess the complex multiple equilibrium reactions with phosphorous we need to have a firm grip on the concentrations of the chemical constituents in the water matrix used for the experiments.

Different types and brands of 0.45 µm pore size filter papers were used to filter the water (see Chapter 4.3.1.3.1). For the P fractionation the samples were in addition filtrated with 0.7 µm pore size. Information regarding what filter paper that was used to filter the sample for the determination of the various parameters is given in Appendix, Paragraph 8. Standard deviation and number of replicates used for the measurements of the parameters are given in the same place.

### 5.1.1 pH, conductivity, alkalinity and particulate matter

Table 5-1 gives the results for pH and conductivity, measured on the same day as sampling, and the temperature of the sample when these parameters were measured. The pH and conductivity measurements at the start of the experiments are also given in Table 5-1 for comparison to see the effect of storage. Alkalinity and particulate matter are also shown in Table 5-1.

The pH was close to neutral in the Agricultural, Watershed and Lake samples, which is similar to previously reported data (Parekh, 2012; Skarbøvik et al., 2011). A higher pH (up to 10) has been observed in Lake Vansjø during periods of severe algal blooms. The pH in the sample from the forested catchment was 4.9, which is in the higher range of what that is previously measured in water samples from this stream (Mohr, 2010; Parekh, 2012; Weldehawaria, 2013). (Parekh, 2012) found a median pH of 4.4. The higher pH is opposite of the expected as pH is normally lower during high flow. Melt water and large amounts of rain can have caused a dilution of the stream water, especially as the water flow probably had been high for some hours at the time of sampling. The pH of the forest sample changed to 5.6 by the addition of azide. This change is not seen in the other, more strongly buffered samples.

In the water-mixing study of Shekobe (2012), the water samples from the Agricultural and Forested water samples had pH 6.5 and 4.5, respectively. The difference in the pH between that study in the experiments performed here is thought to have caused a change in the charge of the monomeric Al, and can have been a main cause for different results.

The observed increase in conductivity prior to the experiments was caused by the addition of sodium azide. The increase is greater for the watershed sample which was added 0.02 % w/w sodium azide and used for the sorption-desorption experiment, while the samples for the water-mixing experiment were added 0.002 %.

*Table 5-1: pH, conductivity, temperature, alkalinity and particulate matter of all the water samples. The watershed sample is used for sorption-desorption experiments, and the three others are used for water-mixing experiment.*

| | **Watershed (Hobøl)** | **Agriculture (Støa)** | **Forest (Dalen)** | **Lake (Vansjø)** | **Unit** |
|---|---|---|---|---|---|
| Temperature | 22.8 | 23.3 | 23.0 | 21.6 | °C |
| pH (sampling) | 6.8 | 7.2 | 4.9 | 7.1 | |
| pH (experiments) | 6.6 | 6.8 | 5.6 | 6.7 | |
| Conductivity (sampling) | 82 | 124 | 32 | 81 | µS/cm |
| Conductivity (experiments) | 360 | 135 | 53 | 95 | µS/cm |
| Alkalinity | 0.23 | 0.85 | n.m. | 0.29 | mmol/L |
| TSS 0.7 µm GF | 20 | 23 | 4 | 4 | mg/L |
| TSS 0.45 µm M | 20 | 25 | 4 | 4 | mg/L |
| TSS 0.45 µm S | 23 | 29 | 3 | 4 | |

*n.m.: This measurement was chosen not to be done for this sample as it was assumed to be close to zero.*

Total suspended solids (TSS) were measured with three different filter papers, but the filter papers did not retain significantly different amounts of particles.

The average TSS concentration in the period October 2012 to October 2013 was 35 mg/L in the Watershed stream (sampled by Kure, a few km upstream from the sampling point used here), 33 mg/L in the Agricultural stream and 3 mg/L in the Forested stream (Skarbøvik, Haande, & Bechmann, 2013; Skarbøvik et al., 2014). It is surprising that the TSS in the samples used here is comparable to what is found in the streams, as the samples were left for sedimentation for so long.

### 5.1.2 Organic matter

The concentration and characteristics of organic matter are given in

Table 5-2. The DOC concentrations shown in

Table 5-2 are the average of two measurements performed with a three months interval to observe if the samples changed during storage, see Appendix, Table 8-3. The concentrations were slightly lower upon the second measurement: about 1 % lower for the Lake and Forest samples and about 10 % for the Watershed and Agriculture samples. Thus, some biological material seemed to degrade upon storage.

The forested sample has about twice the amount of DOC compared to the other samples. This is also indicated by the highest absorbance at 254 nm among the filtered samples. However, the Watershed, Agricultural and Lake samples all have similar DOC but quite varying absorbencies at 254 nm implying different physical characteristics of the DOM. The apparent contribution from the particulate fraction to absorbance at 254 nm is small for the Lake and Forest sample, while for the Watershed and Agriculture sample it is slightly over 20 %. This is likely an artefact due to the light scattering by the high concentration of particles in these samples, and not necessarily caused by absorbance of the aromatic carbon in the PNOM. The SAR indicates that the unfiltered Watershed and Agriculture samples have the highest molecular weight. Upon filtering all samples show lower molecular weight, which is expected as the highest molecular weight OM will be removed by the filter. The change is biggest for the Watershed sample, which also had the largest reduction in 254 nm absorbance. The sUVa for the filtered samples shows that the watershed and agriculture samples have the highest aromaticity.

The absorbency at 600 nm was generally very low (most values between 0.003 – 0.013) and consequently uncertain, and are thus not included.

*Table 5-2: Concentrations of dissolved organic carbon (DOC) and the absorbency at 254 and 400 on filtered and unfiltered sample, along with sUVa and SAR.*

| | Watershed (Hobøl) | Agriculture (Støa) | Forest (Dalen) | Lake (Vansjø) | Unit |
|---|---|---|---|---|---|
| **Carbon** | | | | | |
| DOC | 7.3 | 7.9 | 13.1 | 7.5 | mg/L |
| **UV/Vis absorbance** | | | | | |
| Absorbance 254 nm, unfiltered | 0.697 | 0.544 | 0.648 | 0.327 | $cm^{-1}$ |
| Absorbance 400 nm, unfiltered | 0.116 | 0.093 | 0.076 | 0.036 | |
| SAR unfiltered | 6.0 | 5.8 | 8.5 | 9.2 | |
| Absorbance 254 nm, filtered | 0.519 | 0.428 | 0.628 | 0.310 | $cm^{-1}$ |
| Absorbance 400 nm, filtered | 0.052 | 0.056 | 0.072 | 0.028 | |
| SAR filtered | 10.0 | 7.7 | 8.8 | 11.2 | |
| sUVa filtered | 7.1 | 5.4 | 4.8 | 4.1 | mg/Lm |
| Absorbance 254 nm, difference | 0.178 | 0.116 | 0.020 | 0.018 | $cm^{-1}$ |
| Absorbance 254 nm, difference | 0.064 | 0.038 | 0.005 | 0.008 | |

Shekobe (2012) measured higher absorbance of unfiltered samples by 254 nm for the Forested sample (1.5) and lower for the Agricultural (0.181), while the SAR was slightly lower for the Forested sample (8.8) and twice as high for the Agricultural sample (12.0). This indicates that the Forest sample of Shekobe had much higher content of organic matter with slightly higher molecular weight, and the Agricultural sample had lower content of organic matter and much lower molecular weight.

The measurements of the organic content are not directly comparable as Shekobe measured TOC on unfiltered sample, and the samples here were filtered (thus measuring DOC).

### 5.1.3 Aluminium fractionation

The forested water sample has the highest monomeric and total dissolved Al concentrations (Figure 5-1), while the agricultural sample has a higher particulate Al concentration due to higher amount of suspended solids (see Chapter 5.1.1) including clay – inherently containing Al. Higher concentrations of monomeric aluminium (Ala) in water from forested areas are expected due to higher solubility of Al below pH 6 and complexation by the high concentrations of DNOM, as well as some enhanced leaching of Ali by anthropogenic

deposited sulphate acting as a mobile anion. The lake sample has low Al concentrations for all fractions.

The water from the forested catchment had an Alaf concentration of 10.6 µM (the measured Ala concentration is less reliable and thus not used here), which is lower than what was the case during the acid rain period. Ala concentrations of 20-30 µM was measured during high flow in the Birkenes Catchment in Southern Norway in 1984-1986 (Seip et al., 1989), and it is assumed that similar concentrations were found in the Dalen catchment (Forest sample). The measured Alaf concentration is also relatively low compared to what is measured by the present monitoring; Parekh (2012) found a median Ala concentration of 18.6 µM in the Forest stream, but the Forest sample used in the study of Shekobe (2012) had similar concentration as found here (11.6 µM). In the water-mixing experiment, the water sample from the forested catchment was used in the blank experiment as it is to represent today. In the other experiments Al was added to acid rain levels to simulate previous conditions.

The standard deviations in the Al measurements are up to 50 % between days (see Table 8-1 in Appendix).

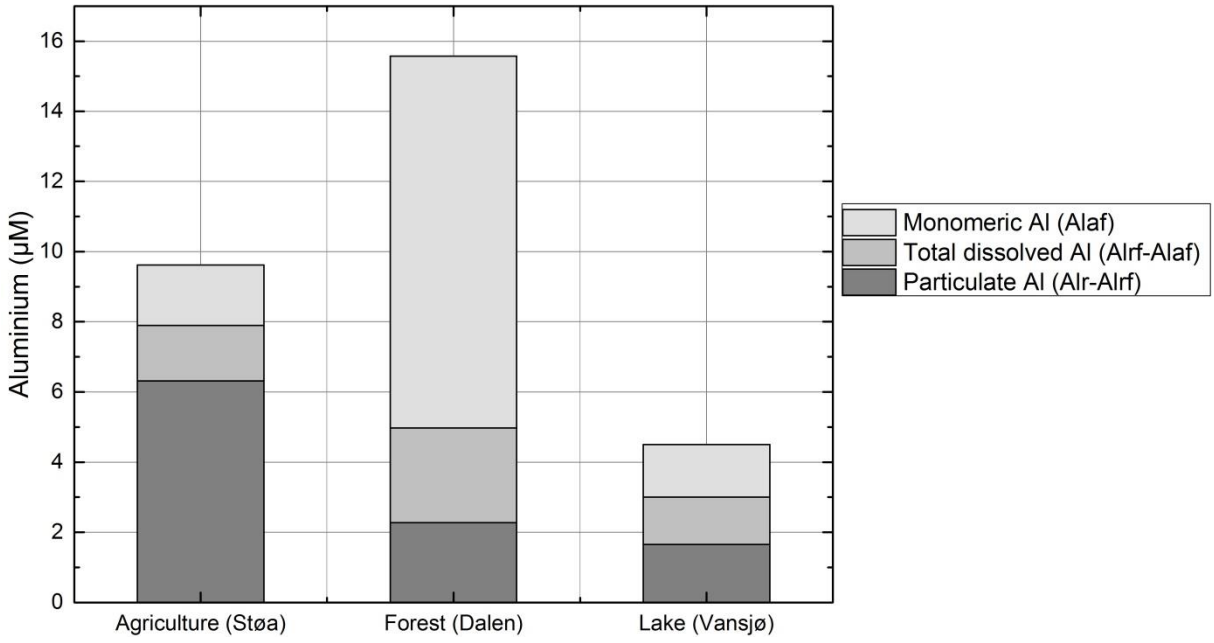


*Figure 5-1: Aluminium fractionation of the samples used for the water-mixing experiments.*

Results for Alof and Alif are not included due to that the pH was above the range in which the fractionation method is applicable (see Chapter 4.3.1.4.2). The Watershed sample was not measured as it was not used for experiments were aluminium was monitored.

### 5.1.4 Major anions and cations

Figure 5-2 and Figure 5-3 show the measured concentrations of major anions and cations. $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$ and $K^{+}$ were measured with both ICP-OES and IC, and the results from the two methods were comparable (see Appendix, Table 8-4). The results from the ICP-OES are higher than the results from the IC for all samples. This is to be expected as the ICP measure the total concentration while the IC only measures the aqueous species. On the other hand as the measurements using the ICP were performed three months before the IC, the effect of storage can have been important. The average of the two measurements is used in the figures. The good agreement between the equivalent sum of anions and cations shown in Figure 5-2 implies good data accuracy.

Figure 5-3 shows that the agricultural runoff is strongly influenced by calcium carbonate, while the water quality in the other three streams is mainly dominated by sea salts ($Na^{+}$ and $Cl^{-}$). The ionic composition and concentrations of the watershed stream appears as a mix of mainly agricultural and forested runoff, which is the case. Furthermore, the composition and concentrations found in Lake Vansjø are similar to that in the watershed stream, which is expected as this stream should represent the catchment as a whole, and is the biggest contributing stream to the lake.

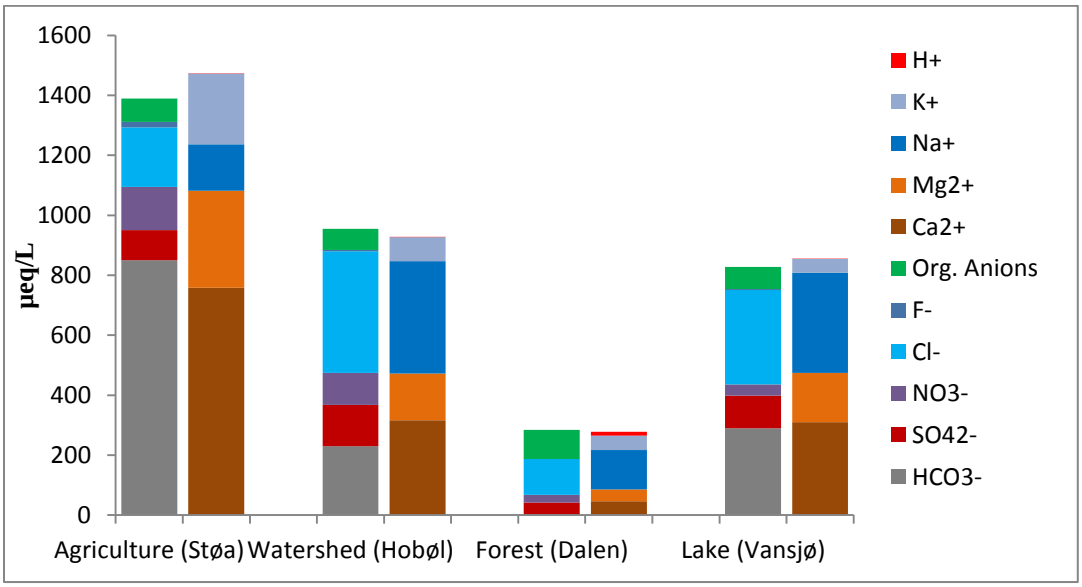


*Figure 5-2: Distribution of major cations and anions in the water samples.*

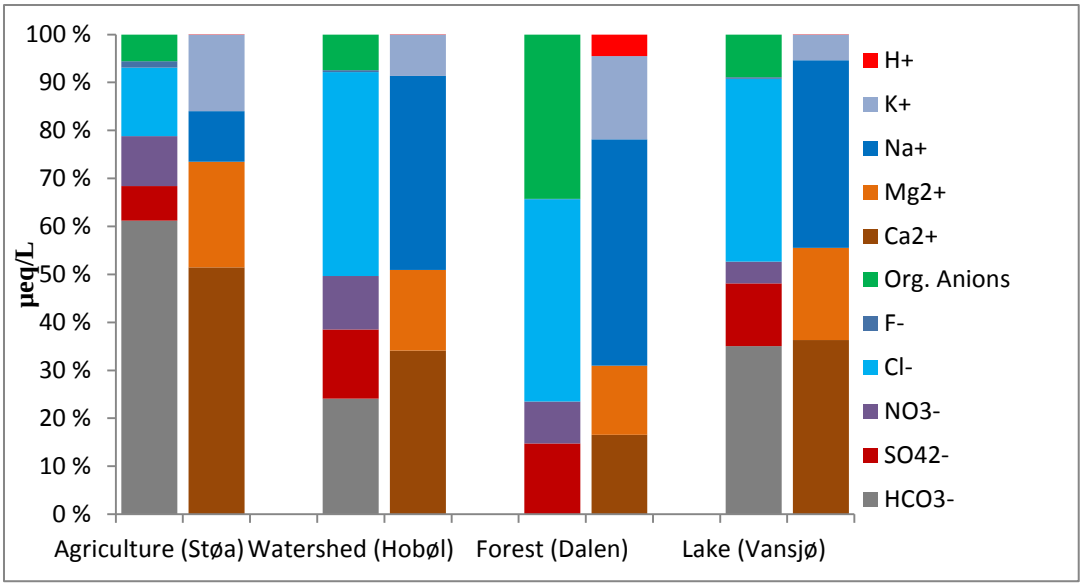


*Figure 5-3: Percentage distribution of major anions and cations in the water samples.*

### 5.1.5 Trace metals

As expected, the iron (Fe) and aluminium (Al) are the most abundant trace elements (Figure 5-4), and all the heavy metals are below µM level (see Table 8-5 in Appendix, Paragraph 8). The total Al and Fe concentrations are highest in the forest sample, due to increased solubility and mobility by complexation to DOM. The Fe concentration in the agriculture sample is the second highest, but might have been much higher upon sampling as iron precipitation was seen during storage for this sample. The soils in the watershed of the Agriculture stream has high Fe content (Opland, 2011).

One of the reasons for measuring the dissolved trace metals was to look for possible interferences for the P measurements by the MBM method. None of the measured concentrations can give interferences in the MBM method (see Appendix, Paragraph 8.10.2)

The Al measurement from the ICP-MS analysis should theoretically be the same as the Alrf (total Al in filtrated sample) in the Al fractionation. For Dalen and Vansjø they are similar (for Vansjø it is the same value), but for Støa the concentration measured in the Al fractionation (spectrometric) is 3 times higher than the concentration measured in the trace metal analysis (ICP-MS). According to the results from the ICP-MS analysis, the iron concentration is ten times higher than the Al concentration in this sample. Iron interferes with the spectral measurement, and is corrected for. However, in this case the correction is more

than 50 % of the absorbance, thus this creates a large uncertainty and can possibly explain the different results from the two methods. Both analyses were performed after several months of storage.

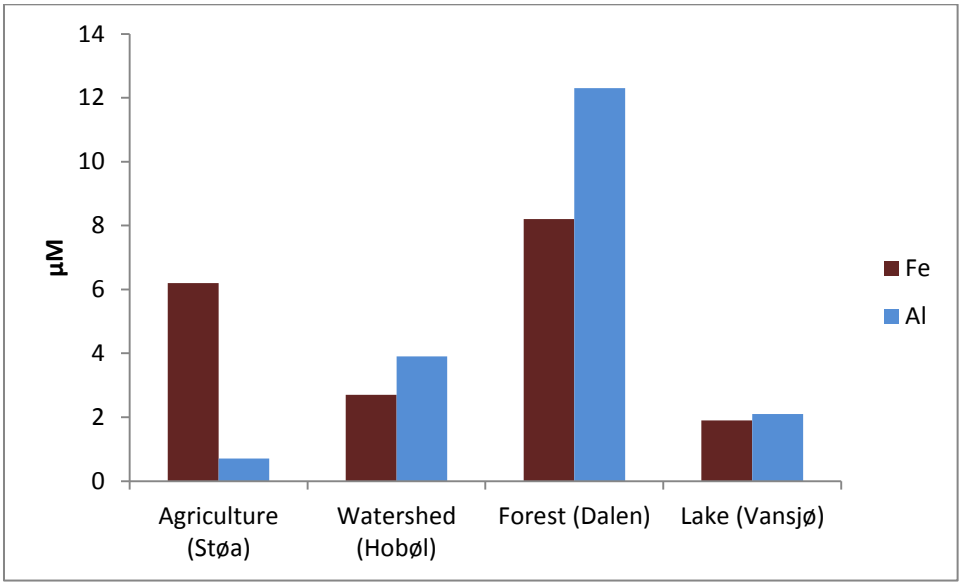


*Figure 5-4: Iron, aluminium and manganese in the water samples.*

The concentrations of Fe and Al are higher in the streams than in the lake. This implies that the ions precipitate out of solution before reaching the lake or in the lake.

### 5.1.6 Phosphorus fractionation is the case here.

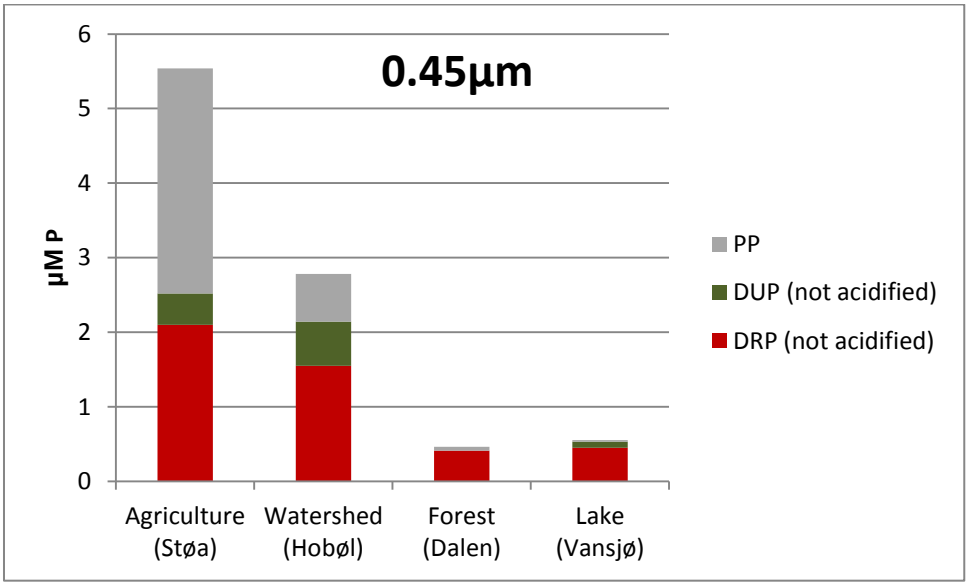


Figure 5-5 and Figure 5-6 shows the concentration of phosphorus (P) fractions in the water samples used in the experiments. As expected the total phosphorus (TP) concentration was

highest in the water from the agricultural catchment. Also the dissolved total phosphorous (DTP), the dissolved reactive phosphorous (DRP) and the particulate phosphorus (PP) are highest in the Agricultural sample, while the dissolved unreactive phosphorus (DUP) is highest in the Watershed sample. The Watershed sample has also quite high concentration all P fractions. This river naturally contains high PP concentration, but as the samples were left for sedimentation before characterization most of the particles were sedimented and separated from the sample. The Agricultural sample has high PP concentration despite the sedimentation of the particles, thus these particles might be smaller in size and have remained suspended. The samples from the forested catchment and the lake have low concentrations for all phosphorous fractions; the Forest has an unexpectedly low DUP concentration compared to the study by Parekh (2012), which might be caused by the quite low concentrations of organic matter in the sample  Quite a large fraction of the TP in Lake Vansjø is found as DRP.

The DTP and DRP are measured on samples filtered through 0.45 µm membrane and 0.7 µm glass fibre filters. Surprisingly, the DTP in the Watershed, Forest and Lake samples are lower in the 0.7 µm filtrate than in the 0.45 µm filtrate. The samples filtered with 0.7 µm pore size were acidified after filtration, before DRP measurement (se Chapter 4.3.1.4.1), which will change the distribution of P between DRP and DUP as well as likely dissolve some colloidal material freeing adsorbed P; the acidification is therefore – as for the difference in filter pore size – expected to give higher DRP concentration for the 0.7 µm sample, and not lower as is the case here.

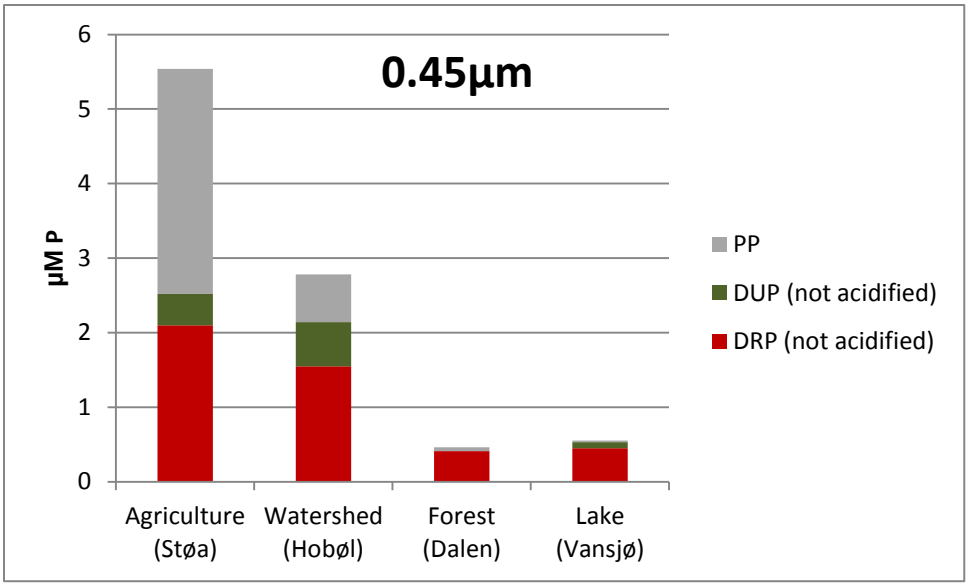


*Figure 5-5: Phosphorus fractionation measured on the water samples used in the experiments, filtered with 0.45 µm filter paper.*

In the hydrological year October 2012 to October 2013, average TP and DRP concentration in the Hobøl River (sampled at Kure) were 2.4 µM and 0.3 µM, respectively (Skarbøvik et al., 2014). The concentration in the Agricultural stream was 5.6 µM TP and 0.8 µM DRP on average, and in the forested stream 0.5 µM and 0.1 µM. These TP concentrations are comparable to what was found in the samples used here, while the DRP concentrations in the samples used here are much higher. This is probably caused by the separation of particles and water by sedimentation before measurement, taking most of the PP away. The high DRP concentrations are expected due to the high discharge at the time of sampling.

In Storefjorden, where the Lake sample is taken mid-September 2013, TP was about 1.2 µM in April 2014, and this was reduced to about 0.6 µM in July to October (Skarbøvik et al., 2014). The DRP started at about 0.6 µM in April, and varied between 0.2 and 0.4 µM in the period from June to October due to assimilation by algae. The PP constituted about half of the TP. This corresponds well with the measured concentrations in the sampled water, and illustrates that we have sampled in the period when the phosphorus concentrations are low due to grazing by algae.

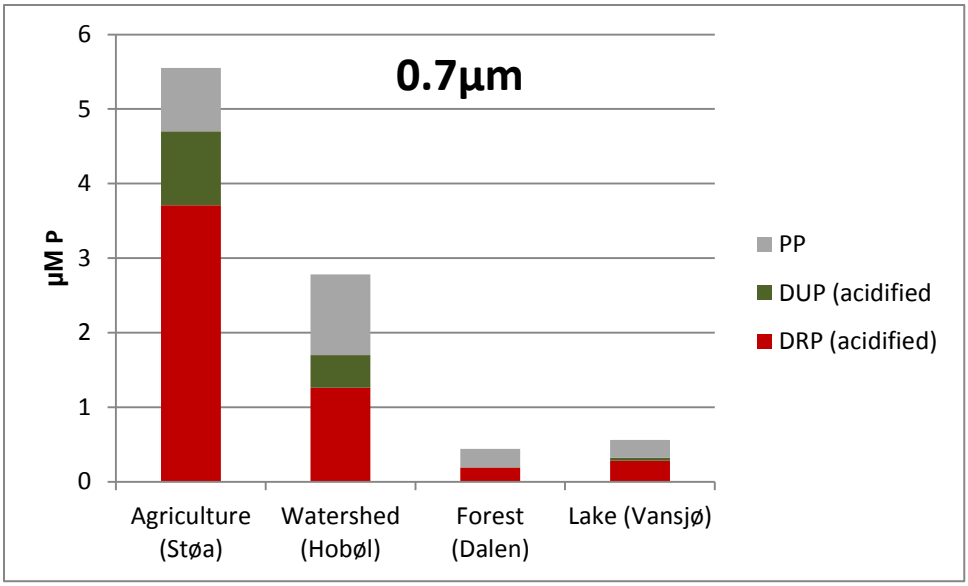


*Figure 5-6: Phosphorus fractionation measured on the water samples used in the experiments, filtered with 0.7 µm filter paper.*

## 5.2 Characteristics of particles used in the experiments

The Watershed particle sample has been used for the sorption-desorption experiments; while the Agricultural particle sample is intended for use in further experiments.

### 5.2.1 Organic content

The content of organic matter is important for sorption properties and thus the ability of the particles to sorb phosphorus.

The organic content as measured by loss on ignition was 5.4 % in the particles from the Watershed stream, and 5.9 % in the particles from the Agricultural stream, thus very similar. The organic content of the particles in the Agricultural stream is similar to previously measured (5.5 %) (Gebreslasse, 2012), while the LOI in the particles in the Watershed stream is about twice as high as found in the Watershed stream sediments (2.9 %).

### 5.2.2 Particle size distribution

Particle size distribution (PSD) and texture is given in Table 5-3. Particles from the watershed stream are mainly silt, and are considered silt loam, while the agricultural particles are coarser with mostly sand, and are classified as loamy sand. The clay fraction – which is so important

for phosphorus sorption – is low in both samples. A finer texture of the Watershed particles than the Agricultural particles were expected as the Hobøl river drains through regions with large clay deposits, while the Agricultural stream drain a watershed located on the Ra end moraine , consisting mainly of sand. The finer texture of the Watershed particles indicate that these will have greater $PO_4$ sorption capacity that the courser Agricultural particles.

Gebreslasse (2012) measured both sediment textures to be silty sand, and found 6.6 and 7.8 % clay in the Watershed and the agricultural sample respectively. He also found more sand in the Watershed sample (50 %).

*Table 5-3: Particle size distribution and texture of the particle samples according to the International soil science society (ISSS) classification scheme. Results are given in volume percent.*

| | Clay (< 2 µm) | Silt (2 – 63 µm) | Sand (63 µm – 2 mm) | Particle texture |
|---|---|---|---|---|
| Watershed | 1.5 | 75.9 | 22.6 | Silt loam |
| Agriculture | 0.6 | 23.0 | 76.4 | Loamy sand |

### 5.2.3 Mineralogy

The minerals in the particle samples and the standard clays are presented in Table 5-4. The detection limit of the method is about 4 %. However, when including minerals below this limit could explain peaks in the signals that were not explained by other minerals, the minerals are listed in the table.

The mineralogy reflects the predominant Precambrian bedrock in the region of which the unconsolidated material is derived. Quarts is the dominant mineral, constituting about half and a third of the weight percent in the Watershed and Agricultural particles, respectively. Albite (or feldspar) is the second most dominating mineral, constituting an additional 24 and 19 %, respectively. Both these primary minerals are from the weathering of the Precambrian bedrock. Other igneous rock-forming tectosilicate minerals, such as Orthoclase and Microcline, were also found in significant amounts in the samples. No Apatite was found in the particles, nor was there any carbonate minerals such as Dolomite or Calcite. The main clay mineral in the Agricultural sample was Kaolinite while no Illite nor Halloysite were detected in neither of the samples. The reference Kaolinite contained as expected mainly Kaolinite (40%), as well as Dolomite and Apatite. The Illite sample mainly contained Illite clays (25%) and Quarts (22%).

*Table 5-4: Mineralogy for the particle samples and standard clays. All results are in percent of the total.*

| | Watershed | Agriculture | Kaolinite | Illite |
|---|---|---|---|---|
| Quartz | 48 | 39 | 4 | 22 |
| Palygorskite | 5 | | | |
| Halloysite | | | 4 | |
| Clinochlore | 12 | 2 | | 15 |
| Berlinite | 2 | | | |
| Dolomite | | | 20 | 14 |
| Muscovite | 3 | 4 | 5 | 4 |
| Kaolinite | | 15 | 40 | 1 |
| Dickite | | | 5 | 14 |
| Apatite | | | 6 | |
| Albite | 24 | 19 | 3 | |
| Illite | | | | 25 |
| Orthoclase | | 10 | 2 | 4 |
| Calcite | | | | 2 |
| Microcline | 7 | 6 | 7 | |
| Gibbsite | | | 4 | |
| Goethite | | 6 | | |

### 5.2.4 Organic and inorganic phosphorus

Figure 5-7 shows the density of organic and inorganic phosphorus in the particles. The two samples are similar, though with slightly higher total P concentrations in the Agricultural sample, and 24 % organic P in both. That there is no large difference in the density of P on the particles, despite that the Støa stream drain only Agricultural soils while the Hobøl stream drains predominant forested areas, is likely due to that the particles in both streams are from agricultural areas as there is little or no particle transport from forests. Moreover, the water chemistry, including the concentration of P fractions, and the physiochemical characteristics of the particles do not differ much between the streams. Large difference in the density of P on the particles is therefore not to be expected. The slightly higher P content of the agricultural sample fits with the slightly higher organic content of this sample, while the smaller particle size of the watershed sample would suggest the opposite.

Previously studied sediments from these sites contained less P (0.08 mmol P /g) (Gebreslasse, 2012) and organic bound P constituted less of the total P (20 % in the Watershed sample and 14 % in the Agriculture sample). The Forested sample was in that study found to have about half of the P density of the others, of which almost 40 % was organically bound P.

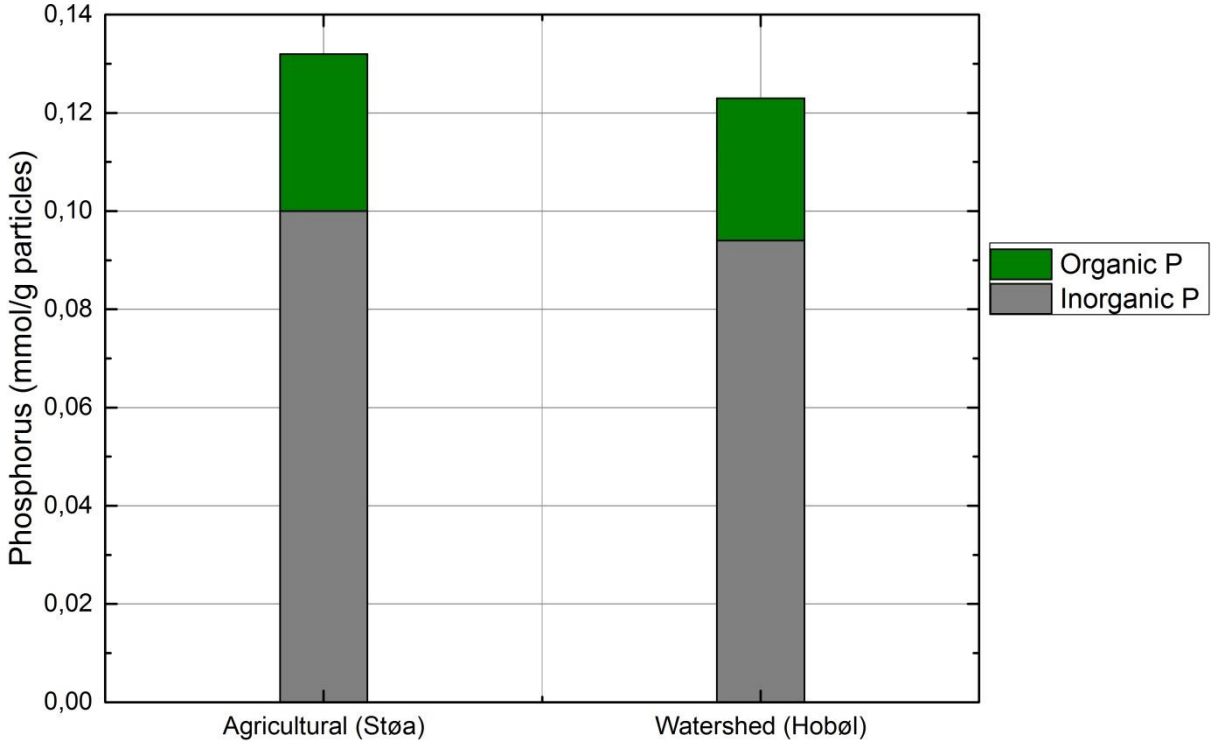


*Figure 5-7: Phosphorus content of the particles used for the sorption-desorption experiment, fractionation into inorganic and organic bound P.*

## 5.3 Sorption and desorption of phosphorus to particles

In the sorption part of the High and Low concentration sorption-desorption experiments (added extra 3.2 and 1.6 µM $PO_4$), P sorption to the particles increased the PP density on the particles with more than 30 %. Only about half of this freshly sorbed P was desorbed during the 4 days desorption experiments. The desorbed phosphorus was mainly released as DRP, and would thus be available for uptake by algae and plants.

The slopes of the logarithmic regression of the changes in P fractions in the desorption part of the experiments are only significantly different from zero in the high concentration experiment (see Appendix, Paragraph 8.5.3), thus only for this experiment we can actually see changes with time.

The DRP measurements in the sorption-desorption experiment were performed on acidified samples, which might have changed the fractionation between reactive (DRP) and unreactive (DUP) dissolved phosphorus, leading to higher DRP.

### 5.3.1 Data treatment: normalizing data with concern to particle concentration

The total phosphorus (TP) should inherently be constant, but was found to vary substantially in the sample aliquots (see Appendix, Paragraph 8.3.3). Conceptually the TP should not be correlated with any of the other P fractions. However, correlations of $R^2 > 0.97$ (see Appendix Paragraph 8.3.1) were found between TP and particulate phosphorus (PP) in the high concentration, the low concentration and the blank experiment (TP was not measured in the filter comparison experiment) during the desorption part. This indicates that the variation in TP was caused by changes in the particle concentration of the aliquots. The particle concentration in an aliquot is very dependent on sample outtake and is difficult to get representative, as also argued by Krogstad et al. (2013). The TP variation seemed random in two of the experiments, while in the high concentration experiment the TP increased with time during the desorption. Thus, this experiment could indicate that there is a change in the particle concentration of the bulk experiment, but as all three experiments were performed in the same manner and the other two had random variation, the variation is thought to merely represent the sample outtake. This is an important difference as an increased particle concentration in the bulk experiment could lead to a change in the equilibrium between sorbed and desorbed phosphorus. As about half of the total volume was removed during the experiment, the particle concentration was prone to change considerably if the sample outtake was not representative. In the aliquot, the short time (about 2 min.) from sampling to filtration is considered not long enough to change this equilibrium.

These large variations in measured TP and thereby PP concentrations do not allow a straight forward interpretation of the data. The measured TP has no consistent (in the meaning of having a trend with $|R| > 0.7$ in the same direction in all experiments) correlation with any of the dissolved P fractions (DTP, DRP and DUP). This indicates that the dissolved fractions are independent on the particle concentration in the aliquots taken out.

To overcome the problem of varying TP concentration, the dissolved fractions are assumed to be representative and TP is set as a constant values (the average of the TP measurements in

that part) in the interpretation of the data in the desorption part. PP is thereby calculated as the differences between this constant TP concentration and the varying DTP concentration, reflecting the changes in equilibrium between dissolved and sorbed phosphorus.

### 5.3.2 Time trends

All time trends (DTP, DRP, PP and DUP) were fitted with simple linear regression after logarithmic transformation of the time. The linear regression does not include the theoretical starting points (time = 0 presented in the right side panel of the Figures below (Figure 5-8, Figure 5-9 and Figure 5-10) showing the changes in density of originally and freshly sorbed PP on the particles. To check if the model is appropriate to describe the data, the plot of the residuals is inspected to check for heteroscedasticity. R-values are given for all time trends in Appendix, Table 8-7.

### 5.3.3 Sorption-desorption experiments with Watershed sample

The density of P on the particles (µmol P/g particles) is chosen for representation of the data because the particle concentration is important for the concentration of dissolved P through sorption-desorption processes, and because it is the effect of the particles that is the main interest of this study.

The originally sorbed density of P is given from the characterization of the PP of the water and change in PP when particles were added to the High concentration experiment. The freshly sorbed P in the sorption part is estimated by the decrease in DTP. Together with the estimated originally sorbed P this constitutes the density of P on the particles at time 0 in the right hand panel in Figure 5-8, Figure 5-9 and Figure 5-10.

The starting concentrations (time = 0) of dissolved P fractions in the desorption part of the High, Low and Blank experiments are not known with certainty as data from these measurements were lost. However, it is known to constitute more than what is desorbed, making the interpretation of the desorption data difficult as we are not capable of using a measured increase in dissolved P for estimating the desorption of P. To achieve a lower starting concentration of DRP in the Watershed water used for the desorption part of the experiment, more potassium alum was used in the preparations for the filter comparison experiment. This makes these data easier to interpret, and the starting concentration for this experiment is also known for the aliquots filtrated with CA filter paper. However, the lower

starting concentration (0.16 µM) makes the experiment not directly comparable to the High, Low and Blank experiment.

#### 5.3.3.1 High P concentration experiment (added 3.2 µM)

##### 5.3.3.1.1 Conductivity and pH

pH and conductivity was measured in the high concentration experiment. During the sorption part, pH increased from 6.8 to 7.9. The reason for this is unknown, but $PO_4$ can have been exchanged for $OH^-$ on the particles, causing pH to rise. Independent of the cause, the increase in pH can have made the particles more negatively charged and reduced their capacity to adsorb $PO_4$.

There was slight increase in conductivity from 334 to 343 µS/cm, which is within the uncertainty of the method. During the desorption part the experiment, pH was varied around 7, and conductivity around 410 µS/cm, but there was no change with time.

##### 5.3.3.1.2 Phosphorus fractionation

In the sorption part of the high concentration experiment, 10.5 µmol P was sorbed per gram of particles. This is a 35% increase in the P loading on the particles and is considered to be substantial. The concurrent reduction in DRP constituted 8.6 µmol of this and DUP 1.9 µmol.

The left panel of Figure 5-8 shows the changes in P fractionation over time during the desorption part. There was a slight increase (about 10 %) in the DTP (i.e. DUP + DRP) with a corresponding decrease in the PP. Both DTP and DRP increased significantly with time (see Table 8-7), something that is reflected in relatively high R values (0.89 and 0.73, respectively). A small amount (1.9 µmol) of DUP sorbed during the sorption part, but desorption of DUP was not measured and the DUP remained relatively constant. The decrease in PP is also significant, but due to the enforced constant TP this fraction is the invers of the DTP fraction and provides no additional information.

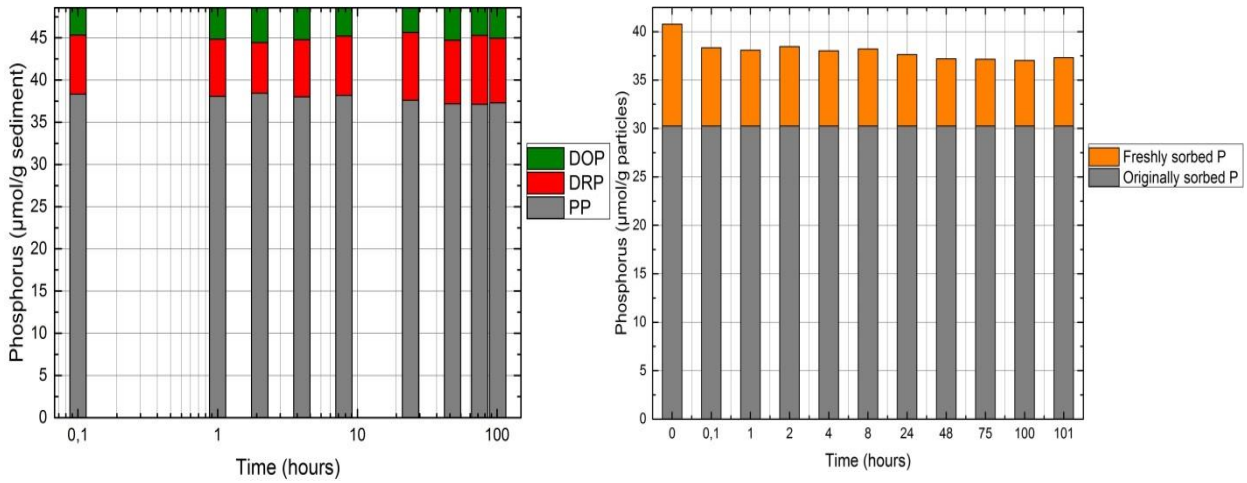


*Figure 5-8: Left panel: P fractionation measured in the desorption part of the high concentration experiment. Right panel: Density of P on the particles in the high concentration sorption experiment, with P represented as the original sorbed P (P bound to the particles before the sorption part) plus the freshly sorbed P (the P sorbed in the sorption part minus the desorbed P in the desorption part).Time 0 is the calculated density of P on the particles added to the water, while time 0.1 represents the first sample filtrated after only few minutes.*

The right panel of Figure 5-8 presents the density of P on the particles prior to and through the 4 day desorption, fractionated into the originally sorbed P (30.3 µmol P/g particles), that was already bound to the particles prior to the adsorption part, and the freshly sorbed P which is the amount of P that was sorbed during the sorption part of the experiment. Time 0 denotes the phosphorous density on the particles (from the sorption part of the experiment) added to the water at the beginning of the desorption part; while time 0.1 represents the first sample filtrated after 5 minutes. Of the 10.5 µmol that were adsorbed, practically half was desorbed again during the time span of the experiment. It is assumed that the freshly sorbed P is more loosely bound and labile than the original, aged PP. This is supported by the blank experiment were no P desorbs. The freshly sorbed P fraction is therefore believed to solely account for the decrease in P density on the particles during the desorption part of the experiment.

An instantaneous desorption of P is apparent at the start of the desorption part of the experiment (the right panel of Figure 5-8). However, the large shift may be due to method uncertainty as the particle concentration in the experiment is not monitored, and loss of particles between the sorption part and the desorption part can thus only be estimated. Such a loss of particles would lead to a reduction in the PP concentration, showing up in the results as decreased density of P on the particles.

#### 5.3.3.2 Low P concentration experiment (added 1.6 µM)

In the sorption part of the low concentration experiment, 9.7 µmol of P per g particles were sorbed. This is slightly less than what was absorbed in the high concentration experiment, and corresponds to a 32 % increase from the originally sorbed P.

The left panel of Figure 5-9 presents the relative distribution in P fractionation during the desorption part of the experiment. The dissolved fractions DTP (R = 0.61) and DRP (R= 0.53) appears to increase – from the first to the last sample there are respective increases of 20 and 90 % – but the slope of the regression line is not significantly different from zero due to the large fluctuation in the values. It is thus not possible to conclude that there actually has been any time trend (see Table 8-7). The DUP seem to just vary randomly.

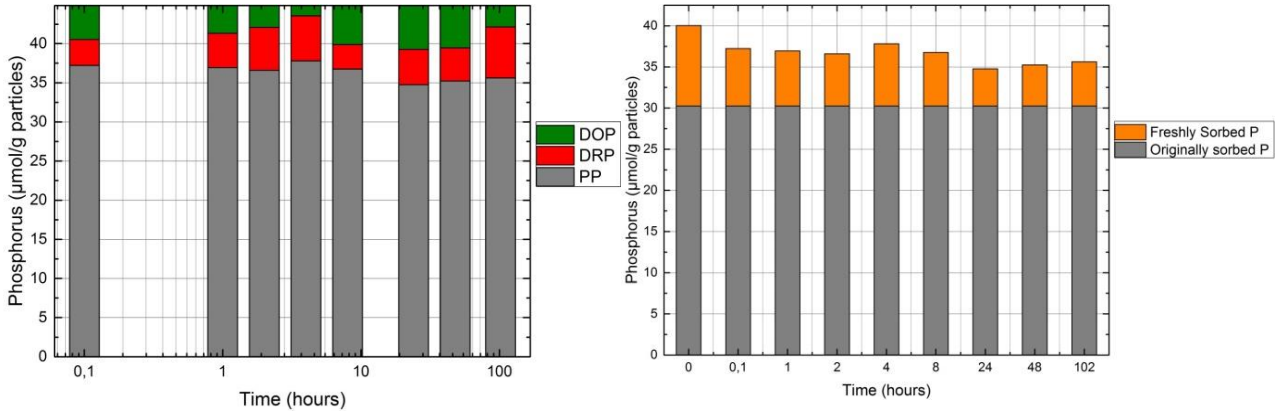


*Figure 5-9: Left panel: Variation in phosphorus fractionation with time in the desorption part of the Low concentration experiment. Right panel: Density of P on the particles in the Low concentration experiment, with P represented as the original sorbed P (P bound to the particles before the sorption part) plus the freshly sorbed P (the P sorbed in the sorption part minus the desorbed P in the desorption part).Time 0 is the calculated density of P on the particles added to the water, while time 0.1 represents the first sample taken out after only few minutes.*

The right panel of Figure 5-9 gives the density of P on the particles during the desorption part of the experiment, with the PP divided into originally sorbed P (30.3 µmol P per g particles) and freshly sorbed P, as explained in Chapter 5.3.3.1. Again about half of the originally sorbed 9.7 µmol P of P per gram particles appears to desorb. However, the estimated decrease is strongly dependent on the estimated values for time 0. If this estimate is wrong, the data might suggest less desorption. This is also indicated by that the fractions do not change significantly with time when looking at the slope of the regression (see Table 8-7 in Appendix), as this is calculated without the estimated first point of the right panel of Figure 5-9.

#### 5.3.3.3 Blank experiment

The fractionation of P with time in the desorption part of the blank sorption-desorption experiment is shown in the left panel part of Figure 5-10. There is no desorption, and this is reflected in the logarithmic regression of P fraction with time where no slopes are found to be significantly different from 0 (see Table 8-7).

There was trouble with the TP measurements in this experiment, as aliquots contained too little particulate bound phosphorus from the start compared to the Low and High P concentration experiments. This is assumed to be due to non-representative sample outtake, and the TP concentration is therefore corrected based on data from the other two experiments.

The changes in the density of sorbed phosphorus are shown to the right panel of Figure 5-10. From the originally sorbed P, calculated from measurements of the particles, there is an increase in sorbed P. This might mean that some phosphorus sorbed during the sorption part of the experiment, which is not expected as the P concentration of the water is the same as when the water was collected and it probably reached equilibrium with the particles during the more than1 month storage before separation. It is more probably an artefact of the method as these results are based on estimations. The calculated freshly sorbed P is anyhow lower in this experiment than in the low and high concentration experiments (the highest value in the left panel of Figure 5-10 is 13 % of the originally sorbed P density), which is expected from the lower P concentration in the sorption part. The data clearly show that there is no desorption of the originally sorbed P.

R-values are negative for all the dissolved fractions, but the correlations are however not strong (-0.51 for DTP, -0.42 for DRP and -0.57 for DUP).

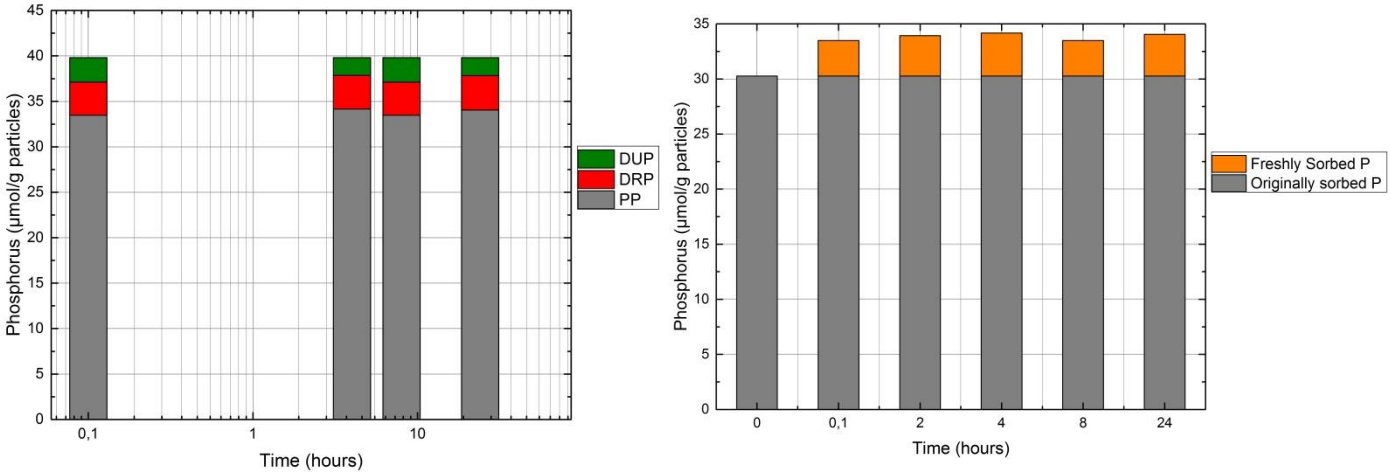


*Figure 5-10: Left panel: Variation in phosphorus fractionation with time in the desorption part of the blank experiment. For the measurements at 1, 2, and 48 h, not all fractions were measured. Right panel: Density of P on the particles PP in the blank sorption-desorption experiment, with P represented as the original sorbed P (P bound to the particles before the sorption part) plus the freshly sorbed P (the P sorbed in the sorption part minus the desorbed P in the desorption part).Time 0 is the calculated density of P on the particles added to the water, while time 0.1 represents the first sample taken out after only few minutes.*

#### 5.3.3.4 Filter comparison experiment (added 1.6 µM)

In this experiment, parallel aliquots were taken out and filtered with two different filters to compare the results of the two different pore seizes: Cellulose acetate (CA) 0.45 µm filter papers and glass fibre (GF) 0.7 µm filter papers.

Figure 5-11 shows the DRP and DUP concentrations in the desorption part filtered using the two filter papers. As in the low concentration experiment (performed with the same P concentration), no fractions changed consistently with time neither for the aliquots filtrated with CA or GF (see Table 8-7). However, the addition of the particles caused the DTP and DRP concentrations in the aliquots filtered by CA filters to increase 32 and 43 % in the 5 min before the first sample was taken out, and additionally 14 and 75 % to the last sample. Thus, there was probably a desorption of P in this experiment. The aliquots filtered by GF filter paper did not change significantly with time (however, measurements of the concentration in the water before the experiment started are missing), and DUP did not change in neither the CA nor the GF aliquots.

DTP, DRP and DUP concentrations were all significantly higher in the aliquots filtrated with the 0.7 µm GF filter paper than in the aliquots filtrated with 0.45 µm CA membrane filter paper, which is expected from the larger pore size of the GF filter papers. Thus, the particulate

fraction sized between 0.45 µm and 0.7 µm constitute a significant amount of particles in natural waters.

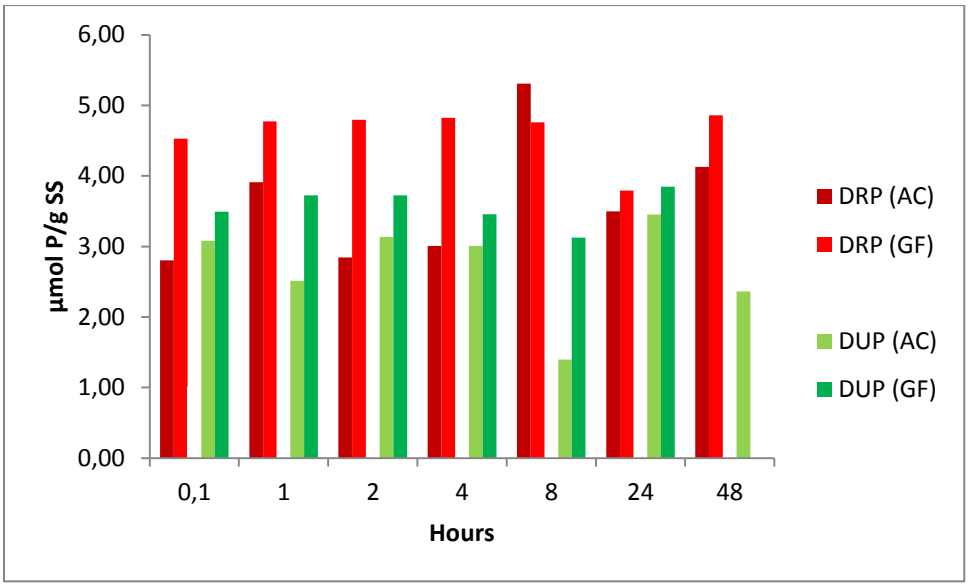


*Figure 5-11: Fractionation of dissolved P in the desorption part of the filter comparison experiment measured with 0.7 µm glass fibre (GF) filter paper and 0.45µm CA membrane filter. For the last data point (48 h), data for the DUP fraction filtered using GF is missing.*

#### 5.3.3.5 Correlation between fractions

The correlations between fractions were investigated to look at how different fractions covariate. This covariation does not imply that fractions changes significantly with time. One example is the correlation between DRP and DUP. DUP was found to be negatively correlated with DRP in all experiments with R varying from -0.5 to -0.9, but this was not reflected in opposite time trends. As DUP is estimated as the difference of DTP and DRP, random errors in the measurement of these will be reflected in the DUP concentration, possibly leading to strong correlations even if none of the constituents change with time. The same argumentation can be used for the correlation of PP with TP and DTP. Thus, there can be correlations between fractions in single experiments that are quite high, but are only due to random measurement errors.

As mentioned in Chapter 5.3.1, the measured TP (i.e. not constant) and PP were strongly and consistently correlated in the desorption part of the sorption-desorption experiments, while no other fractions were consistently correlated with TP. Also, no other fractions were consistently correlated with each other.

DRP and DTP are expected to covariate, as an increase in DRP would inherently lead to an increase in DTP, but this was only observed in three of the experiments (see Appendix, Paragraph 8.3.2), and the two fraction were in fact negatively correlated in the Blank experiment.

PP and DTP are inherently perfectly negatively correlated as they together constitute TP, which is assumed constant. No consistent correlation is found using the measured values for TP that are not corrected for the variation in particle concentration.

#### 5.3.3.6 Paired t-test for the sorption-desorption experiments with watershed sample

A paired t-tests for all P fractions were performed in order to assess if the concentrations of P fractions in the desorption part of the sorption-desorption experiments were significantly different. Thus, to find out if the concentration in the sorption part had a significant effect on the desorbed amount. The concentrations of TP and PP were not considered in these tests due to the uncertainties in the measurements (see Chapter 5.3.1). The filter comparison experiment has not been compared with the High, Low and Blank experiment as the starting concentration for the desorption part was different.

*Table 5-5: P-values for two-sided paired t-test between concentration measurements of the different sorption-desorption experiments performed with the watershed water. P-values below 0.05 mean that the concentrations are significantly different at a 95 % confidence level or higher. Vales above 0.05 are not given*

| Comparison | DTP | DRP | DUP |
|---|---|---|---|
| Blank – Low | 0.04 | | |
| Blank – High | 0.0001 | 0.002 | |
| Low - High | $9 \cdot 10^{-5}$ | 0.002 | |
| 0.45µm and 0.7 µm filter comparison | 0.005 | 0.04 | 0.02 |

The DTP concentrations are significantly different in the High, Low and Blank experiments, while for DRP there is no significant difference between the Low and the Blank (Table 5-5). This might suggest that P was released during the desorption part of the High concentration experiment, and not during the Low concentration experiment, or at least not in amounts that are significantly different from the blank experiment. As about the same amount of P was sorbed in the sorption part of the High and the Low experiments, this was not expected. However, the little additional P that was sorbed in the High concentration experiment might

have been especially loosely bond as the sorption capacity of the particles seemed to be reached already in the low concentration experiment.

The concentration of dissolved unreactive phosphorus (DUP) is not significantly different in the High, Low or Blank experiments, and this is also not expected as this fraction is not seen to change during the experiments.

The filter comparison experiment shows that the 0.7 µm GF filter paper lets through significantly more of all the dissolved P fractions than the 0.45 mm CA filter paper. This implies that a significant fraction of the both the DRP and the DUP is associated with particles in the size range 0.45 to 0.7 µm. It should be stressed that these measurements are taken at the same time from the same experiment, and thus there should be no effects from day to day or experiment to experiment variations.

### 5.3.4 Sorption-desorption experiments with standard clay materials

Blank sorption-desorption experiments were also performed with reference materials illite and kaolinite in Deionized water, i.e. no phosphorus was added in the experiments. The kaolinite gave TP values of about 4.6 µM, of which practically everything was particle bound (PP). DTP concentrations were maximum 0.1 µM, and DRP concentrations were insignificant.

The TP concentration in the water from the experiment with illite were lower (1.0 µM), though almost 20 % of this was as DTP, and 0.1 µM was DRP.

The kaolinite was found to contain 6 % of apatite, constituting part of the P in the kaolinite. The kaolinite has lower sorption capacity than the illite, thus all the P in the kaolinite clay was structurally bound and thus not dissolved The illite has a bigger sorption capacity, and thus contains more desorbable P.

### 5.3.5 Discussion of findings in the sorption -desorption experiments

The Blank sorption-desorption experiment show that there is no desorption of the originally sorbed P, which is an important observation regarding the erosion-reducing abatement actions taken in the Vansjø-Hobøl catchment. The experiment should however be repeated to confirm these data.

The large amount of P that was sorbed to the particles in the High and Low concentration experiments (10.5 and 9.7 µmol per g particles respectively, i.e. giving a 32 and 35 % increase in PP) implies that there is a large capacity for eroded soil material to sorb bioavailable DRP in the streams. The sampling was done on a day with very high DRP concentrations (1.55 µM compared to the 0.3 µM 2013 average), but despite this the particles could adsorb more P. A one-sided focus on abatement actions aimed at reducing soil erosion may thus have a negative effect on the eutrophication problem. This is also supported by that only half of the freshly sorbed P was desorbed when the particles where exposed to water with low P concentration, during the four days the desorption part of the experiment lasted. These results indicate that the particles in the streams can reduce the amount of P available to the algae in the lake: some particles will simply sediment in the stream after sorbing free phosphate, and the particles that arrive in Vansjø might only partly desorb the P they sorbed in the streams.

The added phosphorus in the sorption part of the Low and High P concentration experiments corresponds to a doubling and a tripling in the original DRP concentration, respectively. The particles sorbed about the same amount in the two experiments. This implies that the sorption capacity of these particles was reached already in the Low P concentration experiment.

The filter-comparison experiment shows that the particulate fraction sized between 0.45 µm and 0.7 µm constitute a significant amount of PP in natural waters.

#### 5.3.5.1 Comments to the experiment design

The sorption-desorption experiments with the standard clays showed that 2 hours of sedimentation was not enough for the small particles to sediment, as filtration of the decanted water showed that possibly as much as half of the clay particles were lost in the transition between the sorption part and the desorption part of the experiment. Thus, before decantation of the P rich water in the experiments with the Watershed water, the mix was left overnight for sedimentation to loose less of the small particles. Some particles have probably been lost though, and from observations during the experiment this has been assumed to be about 10 %. However, as the smallest particles are the most important for the sorption processes, the loss of these adds uncertainty to the results. In follow up experiment, the decanted water should be characterized and filtrated for assessment of this loss.

The increase in the ionic strength from the addition of sodium azide favours desorption of P as the competition for the sorption sites increases.

## 5.4 Investigations of water quality change when water from different watersheds are mixed

### 5.4.1 Water-mixing part

Based on the results from the preceding study by Shekobe (2012) an exponential decrease in Al, P and DNOM was expected when the water from the forested stream and the agricultural stream was mixed. In the experiments with added aluminium (Low and High P experiments) the aluminium concentrations decreased immediately, but less than expected, and the dissolved P and OM concentrations changed only slightly.

Results in the mixing part of the experiment are shown as percentage of the conservative mix; a value greater than 100% implies that the concentration of the P fraction has increased due to chemical reactions in the mixed water. Values below 100% imply that the P fraction has had a relative decrease. It should be noted that looking at the results as a fraction of the conservative mix or as the difference from the lake water makes the interpretation vulnerable to errors in this one point.

The change in chemistry with time after mixing is also considered, though the logarithmic regression includes only the measured concentrations after mixing. The start time (i.e. time 0) cannot be included in the logarithmic regression and thus the conservative mix is thus not considered.

#### 5.4.1.1 pH and Conductivity

The Blank experiment was started with pH 5.6 in the Forest water. In the other experiments, the pH of the Forest water was adjusted before mixing: the two Low P concentration experiments to pH 4.5 and the High P concentration experiment to pH 3.8. pH increased considerably in all mixing experiments relative to an estimate of pH based on conservative mix of the $H^+$ concentration. pH stabilized around 7 in the Blank and Low P concentration experiments, and around 6 in the High P.

The increase in pH in the mixed water is caused by the strong buffering capacity of the water from the agricultural area, due to its high alkalinity. The agricultural starting water had a pH of about 7, and completely buffered the acid from the forest water, except in the High concentration experiment where the starting pH was 3.8. This efficient neutralization of acidic water from a forested area has also previously been observed in streams running through agricultural areas (Parekh, 2012).

Conductivity increased relative to the conservative mix in the Blank and the two Low P concentration experiments, while in the High P concentration experiment it decreased. The High P concentration experiment was the only experiment where $PO_4$ was found to be significantly precipitated by Al. Nevertheless, more ions than PO4 and Al must have precipitated in order to explain the decrease in the conductivity from a conservative mix of 137 µS/cm down to 88 µS/cm. The increase in conductivity that was seen in the three other experiments shows that salts dissolved producing ions in solution, which can subsequently lead to formation of particles due to the salt effect. Increased conductivity will also lead to higher competition for sorption sites on particles, and thus possible desorption of phosphorus.

#### 5.4.1.2 Changes in amount and characteristics of organic matter

The temporal fluctuation in absorbance at 254 nm is, as a first approximation correlated, with the DOC content of a sample. In the two Low P concentration experiments and in the High P concentration experiment, the 254 nm absorbance of the unfiltered and filtered aliquots both increased slightly (a few percent) from the conservative mix (Figure 5-12). The large variation in the absorbance of the particulate fraction reflects that this is the smaller difference of two larger numbers. The lack of consistency in the particulate fraction leads to the conclusion that the small increase in the total is caused by the increase in the dissolved fraction. It is unreasonable to assume that the TOC increases during the experiment, however the light-absorbing properties of the water change. There are few significant trends in the 254 nm absorbance after the mixing (see Table 8-13 in Appendix, Paragraph 8.4.1), thus the changes mostly happened before the first aliquot was measured. The Blank experiment did not seem to change, which was also not expected as the Al concentration in this experiment was low.

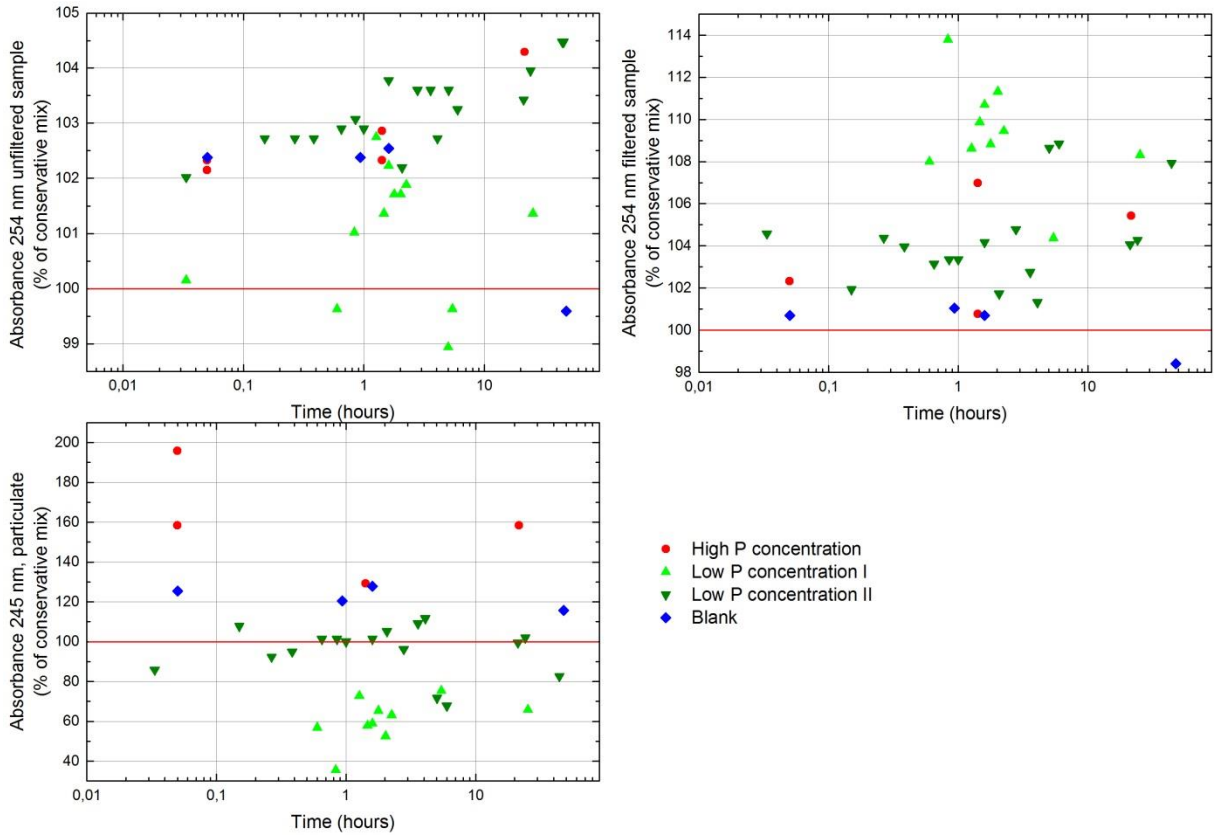


*Figure 5-12: Absorbance at 254 nm as % of the conservative mix for unfiltered aliquots, filtered aliquots and the difference between the two.*

The absorbance at 400 nm in the filtered aliquots increased in all the experiments (4-20 %), also the Blank (Figure 5-13). This increase seemed to be more gradual, and the absorbance of both the Blank and the Low P concentration experiment II increased significantly with time after mixing ($p < 0.05$). Due to trouble with the filtration, the first filtered aliquot of the Low P concentration experiment I was measured after 36 min, which might be the reason this experiment does not show an increasing trend.

In the unfiltered aliquots (Figure 5-13), the Low P concentration experiment deviates by starting below 100 %, something which is probably caused by an erroneously high measurement of the agricultural and/or forested sample water before mixing. Adjusting the value for the conservative mix to the same as for the other experiments causes the absorbance of the first aliquot to be at 100 %. After this correction, the absorbance at 400 nm for the unfiltered aliquots in all the experiments has increased with 5-15 % from the conservative mix. The absorbance at 400 nm in the unfiltered aliquots of the Blank and the two Low P

concentration experiments are all increasing significantly with time ($p < 0.01$). The particulate fraction is again different from the different experiments.

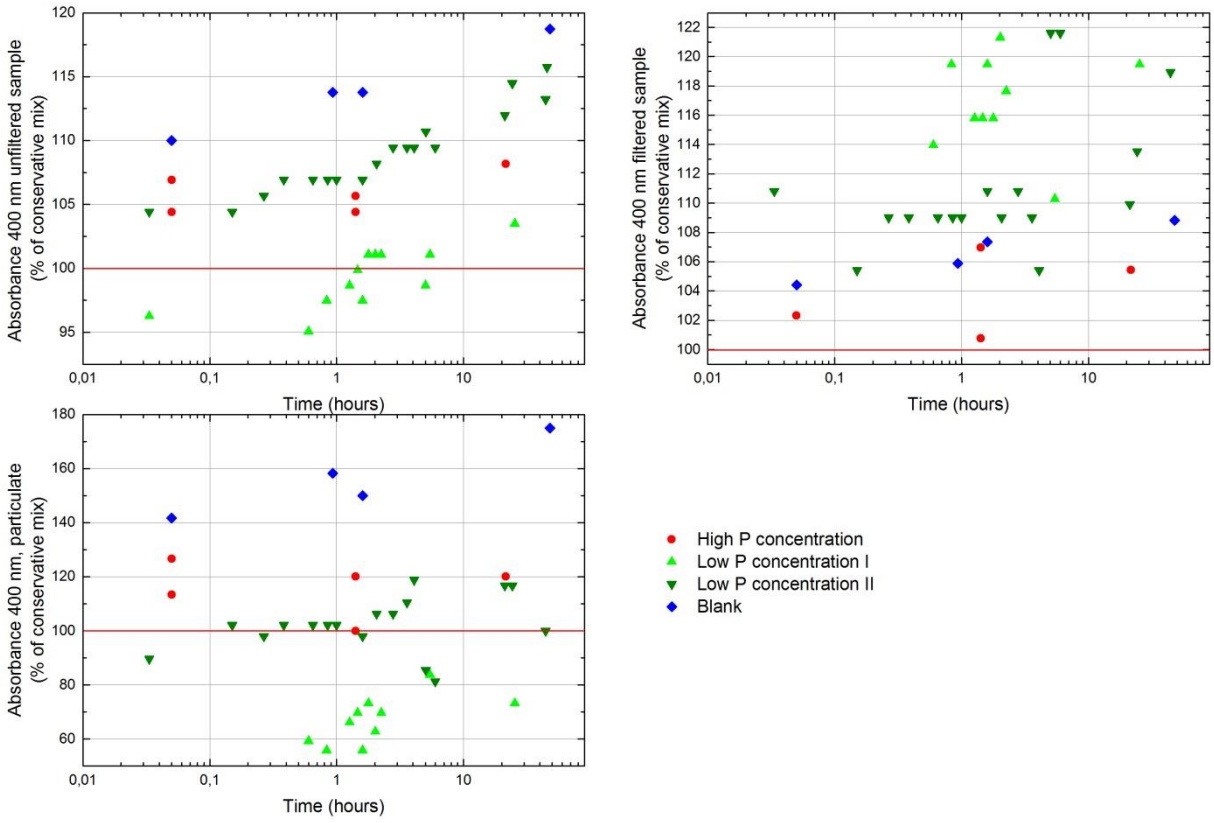


*Figure 5-13: Absorbance at 400 nm as % of the conservative mix for unfiltered aliquots, filtered aliquots and the difference between the two.*

The SAR of the unfiltered and filtered aliquots in the Blank, and the two Low P concentration experiments all decreased significantly with time ($p < 0.05$), and also relative to the conservative mix (Figure 5-14). The unfiltered aliquots in the Low P concentration experiment I deviated from the other experiment and this is again possibly caused by an erroneously high conservative-mix estimate for the 400 nm absorbance.

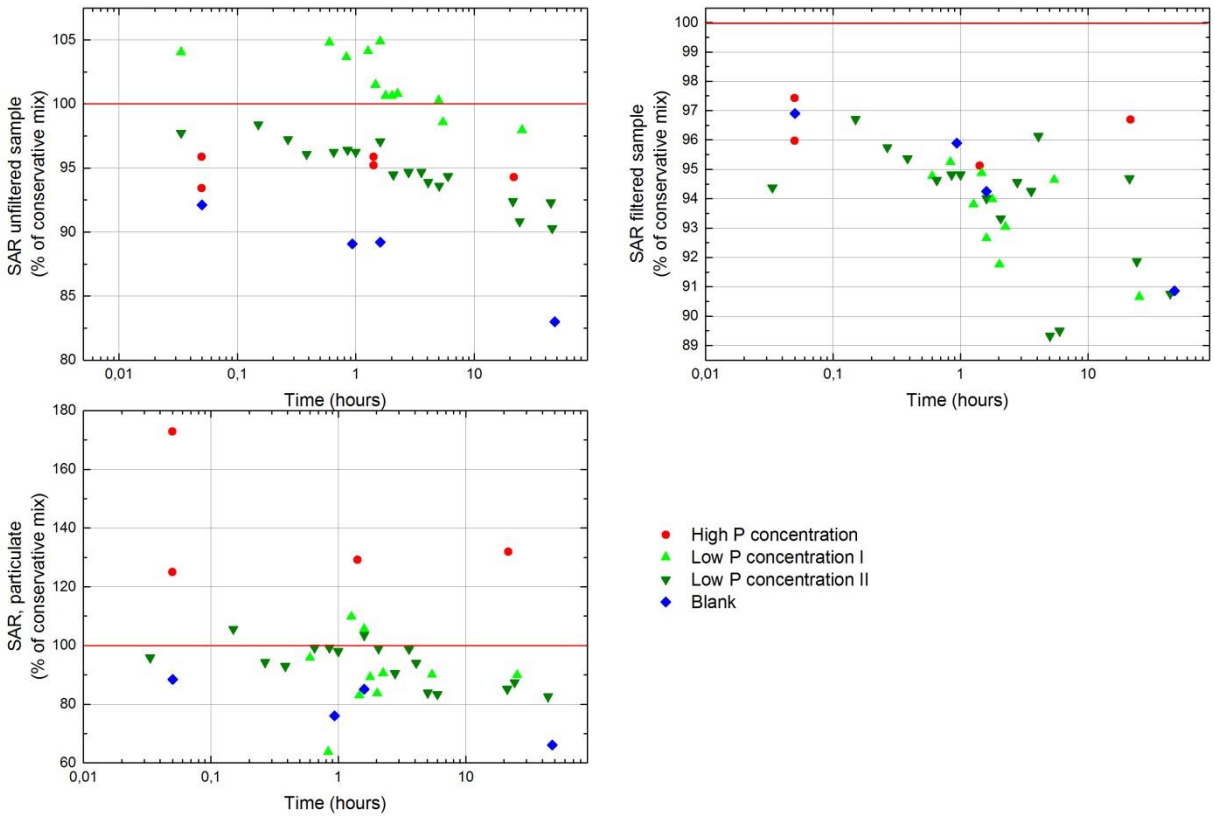


*Figure 5-14: SAR as % of the conservative mix for unfiltered aliquots, filtered aliquots and the difference between the two.*

The changes in the SAR indicate that the molecular weight of the dissolved natural organic matter (DNOM) increased in all the experiments. This change seemed to be independent of Al, as it was also observed in the Blank experiment where no Al precipitated (see Chapter 5.4.1.3). The higher ionic strength and the concentration of $Ca^{2+}$ in the mixed water compared to the forest water reduces the solubility of organic matter and can have caused the organic matter to aggregate and form colloids. As the dissolved fraction did not decrease, there was no formation of particles greater than 0.45 µm.

The use of different filter papers for the Low P concentration experiments compared to the Blank and High concentration experiments does not seem to have caused any difference in the observed trends.

The High P concentration experiment was performed around pH 6, lower than the other three experiments which were performed around pH 7. This was expected to cause an increased precipitation of organic matter (see Chapter 3.2.2). The observed effect of the different pH values is however rather unclear. The most apparent differences between the High P concentration experiment to the other experiments lie in the particulate fraction with increased absorbance at 254 nm, and an apparent *reduction* in the molecular size.

#### 5.4.1.3 Changes in dissolved monomeric Aluminium

In the three experiments where Al was added (the two Low P and the High P experiments) there was a 22 to 26 % decrease in the Alaf fraction in the first aliquots relative to the conservative mix (Figure 5-15). The concentration of Alaf is negatively correlated with time for all four experiments, however this correlation is not necessarily strong or significant (R varies from -0.14 to -0.84, see Table 8-13). Thus, some Alaf precipitated, but this mostly occurred immediately.

The Blank experiment, which was not spiked with aluminium, had neither a reduction relative to the conservative mix (Figure 5-15) nor a significant downward trend for the aliquots taken out with time (Table 8-13). Thus, on a day where the field conditions are like the sampling day, there probably will be no precipitation of Al when water from a forested catchment is mixed with water from an agricultural catchment.

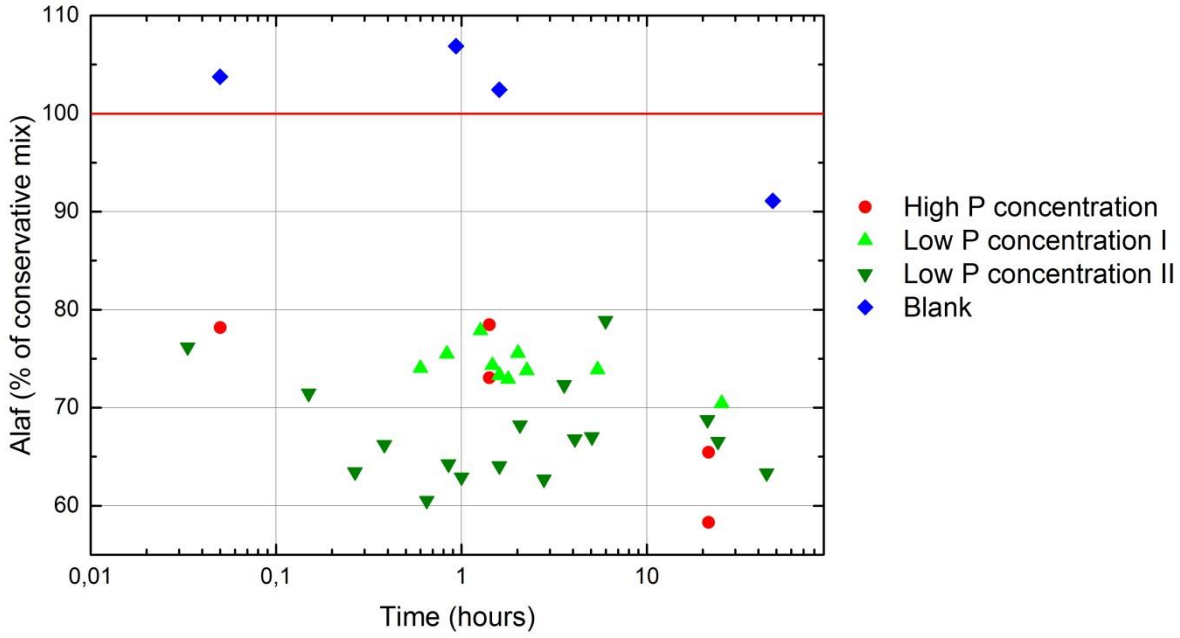


*Figure 5-15: Alaf concentration in the mixing part of the water-mixing experiment, as percent of the conservative mix. The red line at 100 % represents the conservative mix.*

The theoretical speciation of monomeric Al with pH and the pH of the experiments are shown in Figure 5-16. Changes in the Alof and Alif fractions are mainly reflecting the changes in the charge of the dissolved monomeric aluminium at the experimental pH, as discussed in Chapter 4.3.1.5. The measurement of Alof represents the negative and neutral species, and Alif the positively charged species. At a pH close to 7 as in the Blank and two Low P concentration experiments, about 90 % of the dissolved monomeric Al will exist $Al(OH)_4^-$. The negative charge means that the Al will be less efficient in attracting the phosphate anion

than below pH 6.3 where the greater part of the dissolved monomeric Al will be positively charged. The High P concentration experiment was performed around pH 6 where about 60 % of the monomeric Al exists as $Al(OH)_2^+$, and the Al thus more efficiently attracts phosphate. This is a possible explanation of why PP was formed in the High P concentration experiment and not in the Low P concentration experiments (see Chapter 5.4.1.4) despite a clear formation of particulate Al in all the three experiments.

Alof and Alif were monitored in the Blank (the experiment with no additions) and in the High P concentration experiment (added both Al and P). In the Blank experiment, the Alof decreased significantly ($p < 0.05$) with time, while Alif had a non-significant increasing trend ($R_{Alof} = -0.99$ and $R_{Alif} = 0.77$). The same was seen for the change from the conservative mix with a decrease in Alof and an increase in Alif. Considering the pH increase from 5.6 in the forest water to about 7 in the mix, one would expect the opposite to happen. The concentration of Alaf remained constant in this experiment, and a change from negatively and neutrally charged species to positively charged species was not expected.

In the High P concentration experiment, the concentration of both Alof and Alif showed negative time trends ($R_{Alof} = -0.76$ and $R_{Alif} = -0.87$), however the changes were not significant ($p > 0.1$). Compared to the conservative mix, the Alof increased and the Alif was immediately reduced to a third. Considering the pH increase from 3.8 in the forest water to around 6 in the experiment mix, this increase in neutrally and negatively charged species (constituting Alof) is expected.

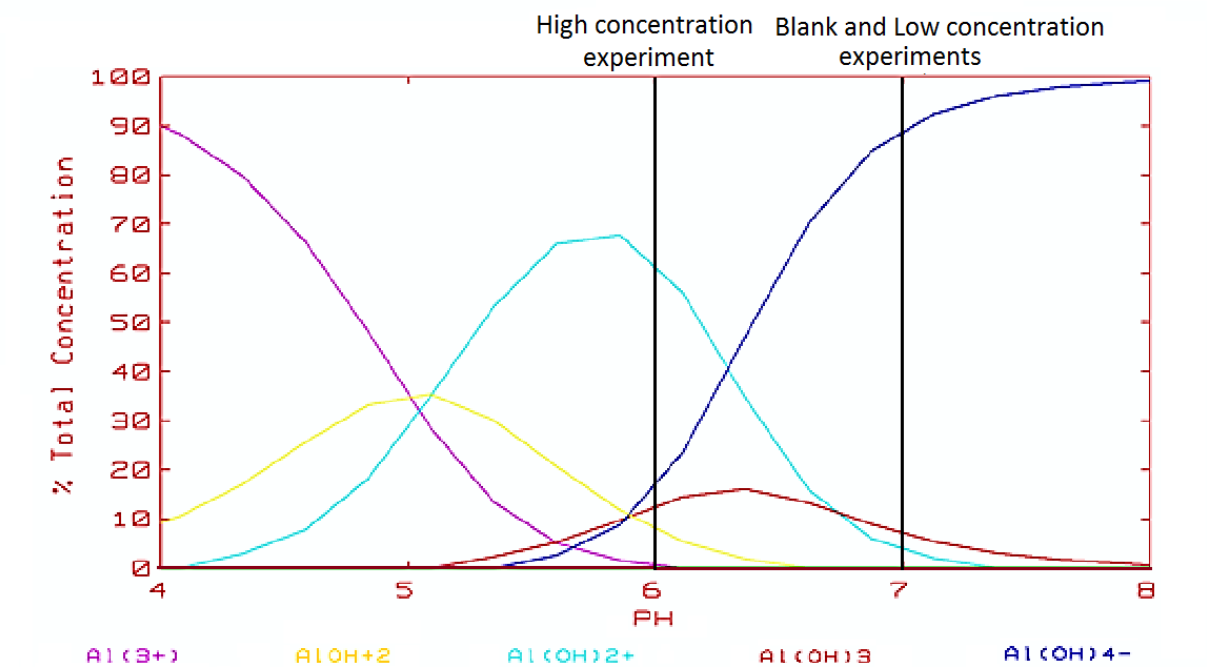


*Figure 5-16: The speciation of monomeric Al with pH. The approximate pH of the experiments is shown with black lines.*

#### 5.4.1.4 Changes in phosphorus fractions

The concentrations of the (non-radioactive) P fractions in the mixed sample of the experiments added Al differed from that of a conservative mix (Figure 5-17), though no clear trends in the P fractionation were observed with time after mixing (Table 8-13 in Appendix) This means that the changes occurred already before the first aliquot was measured, or the changes were too small to be detected with the MBM method.

The concentration of PP was expected to increase and the concentrations of DTP, DRP and DUP were expected to decrease upon mixing of water. Studying the concentrations relative to the conservative mix (Figure 5-17) it appears instead that the opposite occurred, except for the High P concentration experiment. For the Blank and the two Low P concentration experiments, the PP *decreased* relative to the conservative mix and the DTP *increased*. This indicates that P was not co-precipitated with Al to significant extent, and that instead there was desorption from the already particulate bound phosphorus from the Agricultural sample. An increase in PP and decrease in DTP was seen in the experiment with high P concentration. This suggests that the high DTP concentration (8.7 µM) caused the equilibrium with the particles to change to sorption, or a significant amount of P to co-precipitate with Al. However, this may also reflect the lower pH in the High P concentration experiment; this

experiment was performed at a pH of about 6 while the other experiments had circumneutral pH. The monomeric Al is positively charged by this lower pH, and has thus a greater affinity for the phosphate anion. This indicates that the pH can – at least partly – explain why the expected formation of PP was not seen.

The concentration of dissolved unreactive P (DUP) increased relative to the conservative mix in all experiments, also in the high concentration experiment where the DTP decreased. This indicates formation of P-containing colloids smaller than 0.45 µm. A decrease in DRP is apparent in two of the experiments. DRP is thus likely converted to DUP in these experiments. The reason there is no decrease in DRP in the two other experiments is probably the concomitant desorption of P from the particles. The newly formed colloidal DUP can over time mature into PP as the colloids grow. The overall effect is a decrease in bio-available phosphorus.

For all fractions, the Blank experiment has small changes relative to the conservative mix. This indicated that there are no changes in the P fractionation when no extra Al is added.

The concentrations of DRP and DUP changed consistently in the Low and High P concentration experiments, indicating that the use of different filter paper and different method for measuring the DRP samples in the Blank and High concentration experiment did not cause any qualitative differences in the results.

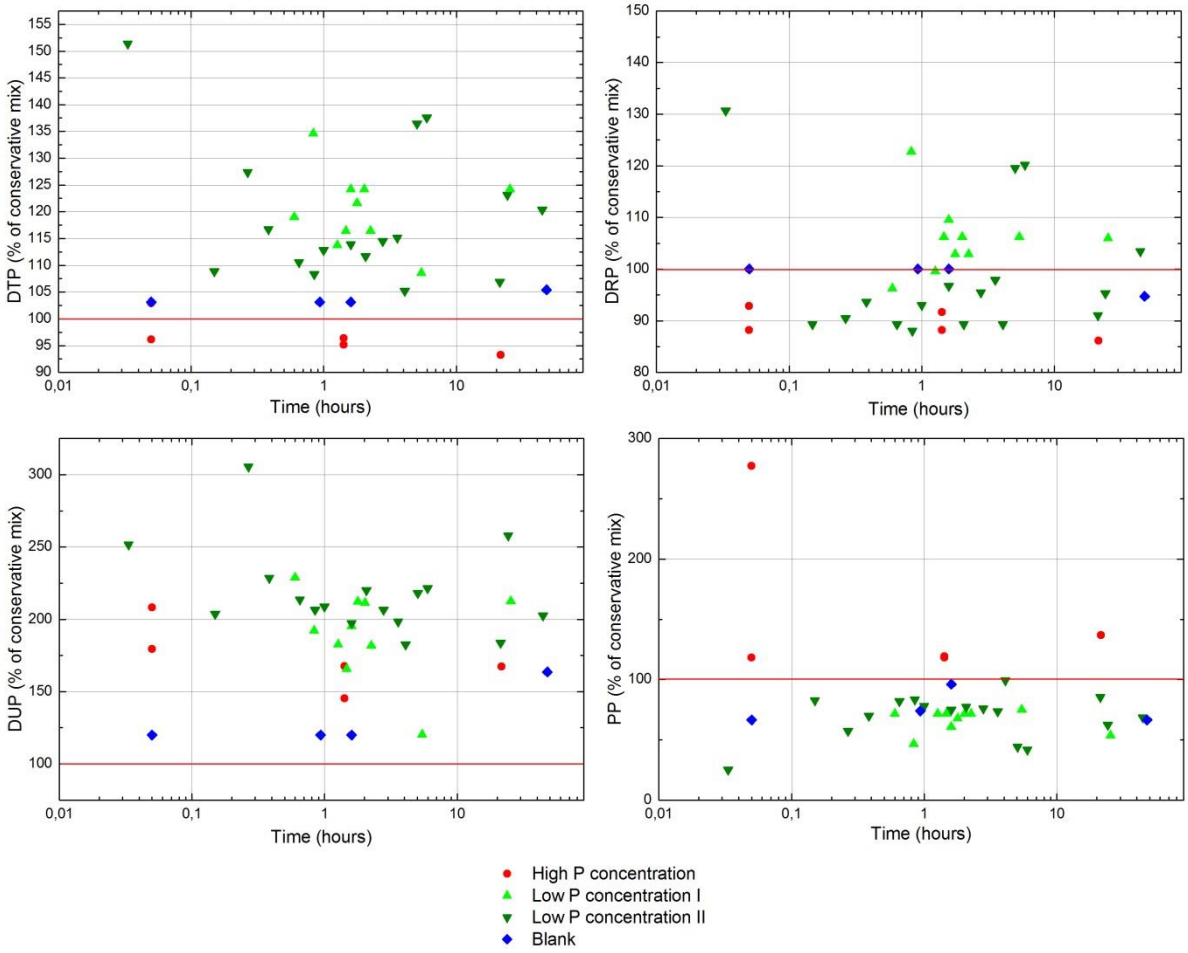


*Figure 5-17: Percent change in different phosphorus fractions in the mixing part of the mixing experiment relative to a conservative mix. The red line indicates the concentration of the conservative mix (100 %)*

The radioactive phosphorus fractions had consistent trends in the Blank and the two Low P experiments. The sum of dissolved and particulate $^{32}P$ is constant through the experiments, supporting that the measurements are correct.

The particulate fraction increased to about 20 % from the conservative mix of 6 % or lower (Figure 5-18) ($p < 0.1$), and the dissolved fraction decreased ($p < 0.05$). Note that this was also seen for the Blank experiment where there was no precipitation of Al. Thus, it appears that the $P^{32}P$ was associated with already existing particles (see Chapter 5.4.1.3). This means that the decrease in dissolved, radioactive phosphorus seemed to be caused by isotopic exchange with the radioactive P replacing the already sorbed (inactive) P in an equilibrium process. The change in the characteristics of the organic material indicated formation of colloids possibly caused by the high ionic strength and $Ca^{2+}$ concentration in the mix

compared to the Forest water. $^{32}P$ associated with these newly formed colloids would however appear as dissolved as the colloids were too small to be filtered out.

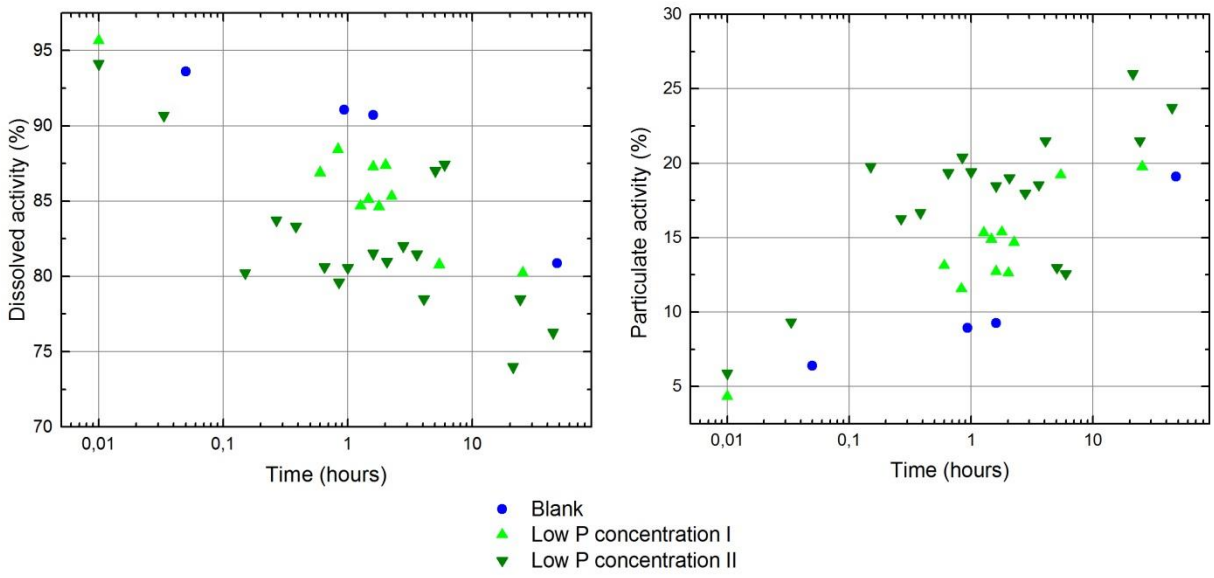


*Figure 5-18: The percentage of the radioactive phosphorus being dissolved and particulate.*

### 5.4.2 Desorption part

In the desorption part of the mixing experiment the filter containing particles from the mixing part of the experiment was exposed to lake water from Vansjø, containing relatively low concentrations of phosphate (Figure 4-9). The desorption part was performed with filter papers from the Blank and the two Low P concentration experiments. The Blank experiment is used as reference in which only two aliquots were measured.

Total and dissolved concentrations of several chemical constituents increased in the water due to detachment of particles from the filter paper as well as dissolution of and desorption from the particles: The concentrations of PP increased, all radioactive P fractions increased, and both dissolved and total OM fractions increased. The concentration of Al fractions generally did not change. Thus, Al that was precipitated in the mixing part of the experiment did not dissolve again, as was expected since the pH was similar in the two parts of the experiments.

The changes in the concentrations of P, Al and organic matter during the experiment are presented as the difference to the concentrations of the Lake water. This is done to emphasize the change. The absolute change is given instead of the relative as the actual released amount of P, Al and organic matter are of main interest.

It would, however, be interesting to look at the desorbed constituents as fractions of the total amount on the filter paper. The absolute amount of the different analytes on the filter paper is however not known, as it was difficult to estimate due to that the filter paper got clogged and retained a larger part of the P and NOM than in the aliquots measured in the mixing part.

#### 5.4.2.1 Conductivity and pH

Conductivity increased from about 90 µS/cm in the Vansjø water to about 115 µS/cm during the desorption part of the experiment. This reflects that ions were released from the particles on the filter paper. The pH increased from slightly below 7 to a bit above.

#### 5.4.2.2 Changes in amount and characteristics of organic matter

Firstly, it is noted that the Blank experiment stronger absorbencies than the two Low P concentration experiments in all the measurements of the unfiltered aliquot. The Blank experiment was performed with the 0.7 µm glass fibre (GF) filter paper, while the two Low P concentration experiments were performed with 0.45 Millipore (M) filter paper. This difference alone could yield the observed differences in the results. However, the GF filter paper added in the desorption part of the Blank experiment was disintegrating due to shaking, and thus the higher absorbencies in the unfiltered fraction might merely be due light diffraction of the glass fibres in solution. The membrane filters added to the two Low concentration experiments did not disintegrate in the same manner.

The 254 nm absorbance of the unfiltered aliquots of the desorption part of the water-mixing experiment increased relative to the Lake water (Figure 5-19), and also increased significantly with time ($p < 0.05$). The filtered aliquot also increased significantly with time ($p < 0.01$), but the Low P concentration I experiment had a lower absorbance than the Lake water. This might be caused by an erroneously high Lake water measurement before the start of the experiment. As in the mixing part of the experiment, the measurements for the particulate fraction show signs of being the small difference between two greater numbers: the uncertainty simply gets too high.

The increase that was seen in the 254 nm absorbance corresponds to about 5 % increase from the absorbance of the Lake water, and indicates that the TOC of the water increased due to desorption of organic matter from the particles on the filter paper or simply detachment of particles, as expected.

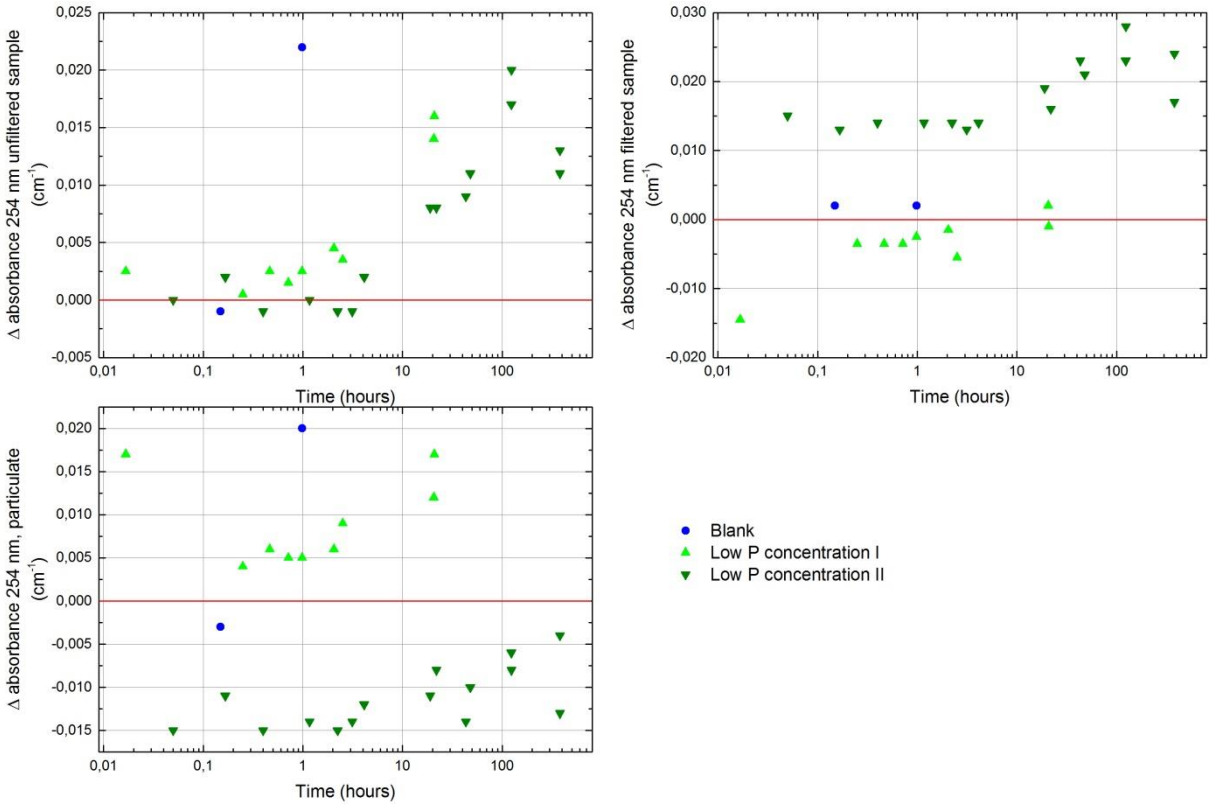


*Figure 5-19: Change in absorbencies by 254 nm for unfiltered aliquots, filtered aliquots and the difference between them. Results are given as the difference in absorbance between the measured aliquot and the Lake water.*

The absorbance at 400 nm increased relative to the absorbance of the Lake water for both the filtered and unfiltered aliquots (Figure 5-20), and showed an increasing trend with time ($p < 0.05$). Once again, the different experiments showed different results for the particulate fraction.

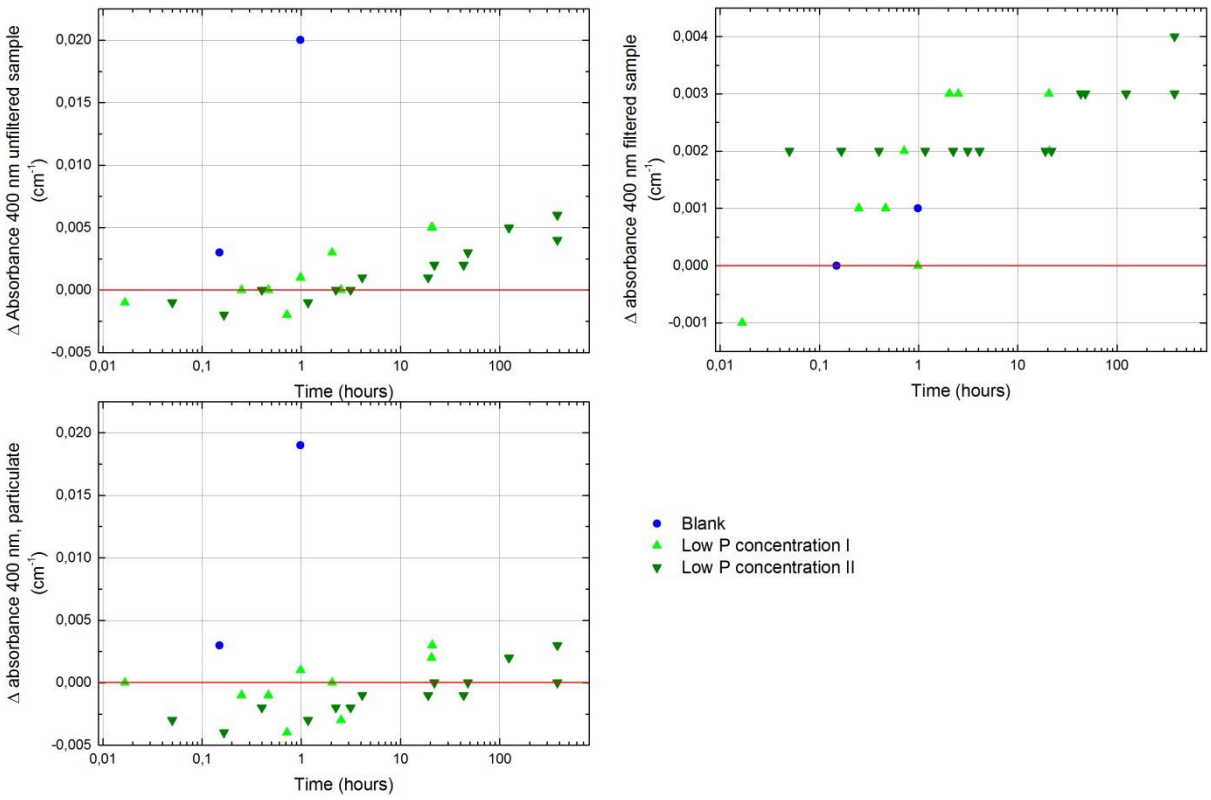


*Figure 5-20: Change in absorbencies by 400 nm for unfiltered aliquots, filtered aliquots and the difference between them. Results are given as the difference in absorbance between the measured aliquot and the Lake water.*

The specific absorbance ratio decreased significantly with time for both the unfiltered ($p < 0.05$) and filtered ($p < 0.1$) aliquots, and also relative to the Lake water. Thus, the molecular size of the organic matter appeared to increase due to detachment or desorption of TNOM from the particles on the filter paper. This was probably mainly particulate organic matter that was originally in either the Agricultural or forested sample. However, during the preparation of the filter paper for the desorption part, the filter paper got clogged and retained a bigger fraction of DNOM (as measured in the filtrate). Thus, newly formed colloids from the mixing part can have been transferred to the desorption part, even if they were slightly smaller than 0.45 µm.

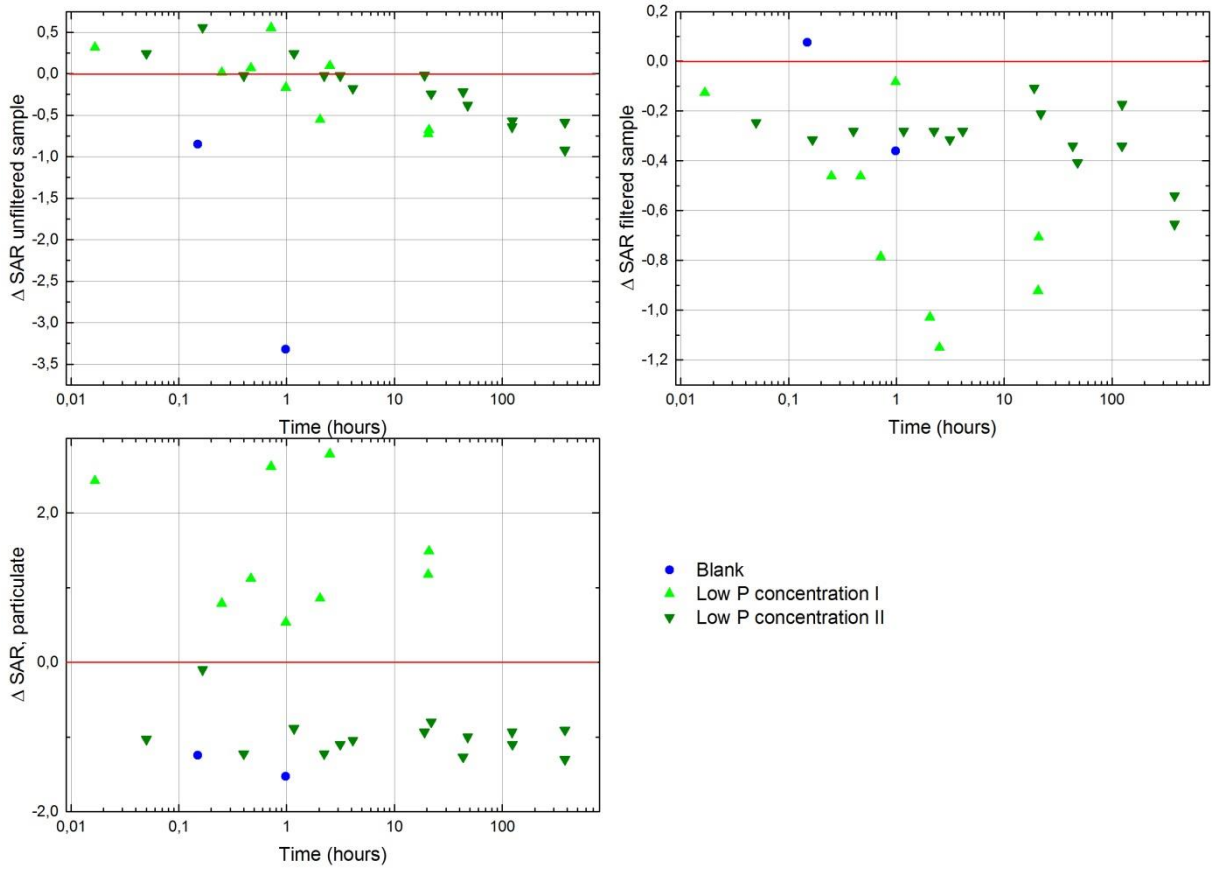


*Figure 5-21: Change in specific absorbance ratio (SAR) for unfiltered aliquots, filtered aliquots and the difference between them. Results are given as the difference in absorbance between the measured aliquot and the Lake water.*

### 5.4.2.3 Changes in aluminium fractions

In general the concentrations of aluminium fractions showed no significant changes during the desorption part of the mixing experiment (see Table 8-14 in Appendix, Paragraph 8.4.1). In the Blank experiment and the Low P concentration I experiment, Alr, Alaf, Alof and Alif were measured, while in the Low P concentration experiment II, Alr, Alrf, Ala and Alaf were measured. In the Low P concentration experiment II the Alr fraction changed significantly ($p < 0.05$), likely due to release of aluminium particles from the filter paper. Detachment of clay particles would lead to an increase in Alr, thus an increase was expected. In the other experiments, Alr was only measured sporadically, and the uncertainty in the measurements was too big to confirm or reject any changes.

### 5.4.2.4 Phosphorus

There was a significant increasing trend in the PP and TP concentrations with time ($p < 0.05$), while DTP was immediately released (Figure 5-22) in the desorption part of the mixing experiment. This indicates that particles containing P were released from the filter paper over

time, likely by mechanical weathering, but that this P mainly remained on the particles. The pool of labile P on the particles bound to the filter paper immediately reached new equilibrium with the DTP in solution.

Interestingly, the increase in DUP occurred before the increase in DNOM. Thus, the released DUP was not bound to organic matter. The DRP fraction increased significantly over time ($p < 0.01$) at the expense of DUP. This implies that the non-labile dissolved P (DUP), possibly formed during the mixing part, was re-suspended immediately from the filter paper and dissociated slowly into labile dissolved phosphorous (DRP).

The Blank experiment deviates somewhat from the two Low P concentration experiments.

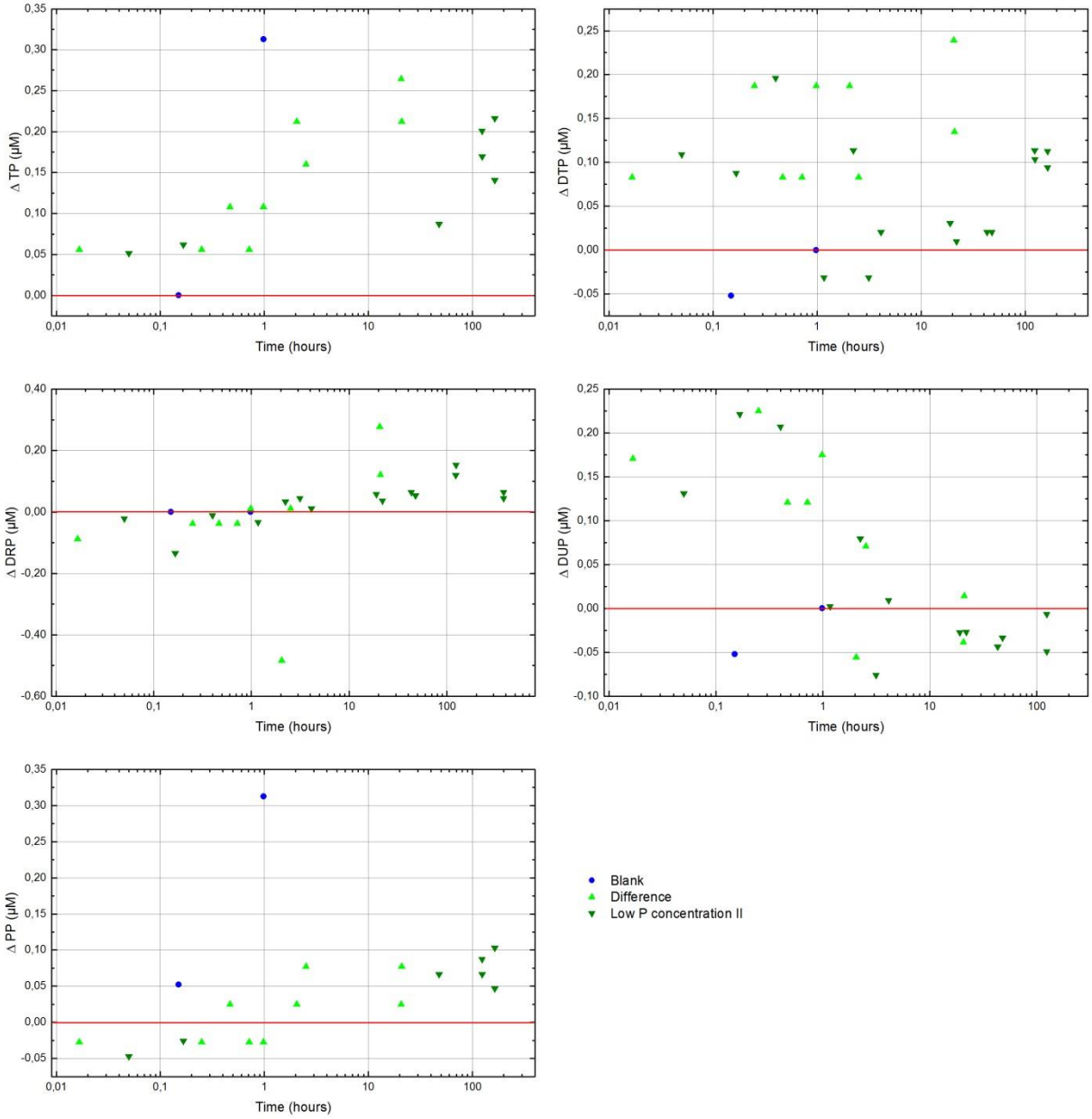


*Figure 5-22: The relative concentration of the P fractions in the desorption part of the water-mixing experiment, as percent of the lake water concentrations. The red line at 100 % represents the lake water concentration measured in the experiment.*

The results from the P measurements with LSC and MBM method were generally the same. Both dissolved and particulate radioactive P increased with time, and the greatest part of the activity was dissolved, except in the Blank experiment (Figure 5-23). The differences in the total released activity between the experiments were caused by different starting activity.

Initially, all the activity was bound to particles. The fractionation between dissolved and particulate activity implies that the P binding to the particles in the streams where the P

concentration is high might desorb again in the lake where the P concentration is low. However, one third of the radioactive P was still bound to the particles after 16 days. The radioactive phosphorus represents the recently sorbed and thus probably loosely bound phosphorus. This indicates that mixing of forest water and agricultural water might be an important sink of P in a catchment.

The results from the Blank experiment comply with the trends from the other two experiments, even if there were no precipitation of Al in the Blank experiment. This indicates that sorption to already existing particles might be more important than processes related to the precipitation of Al.

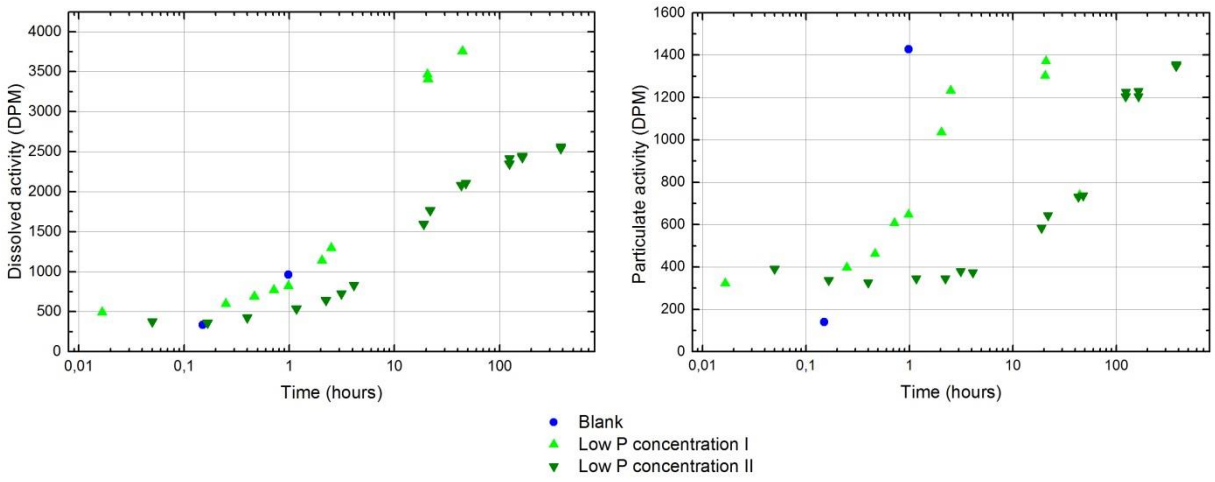


*Figure 5-23: Dissolved and particulate activity in the desorption part of the water-mixing experiment.*

### 5.4.3 Discussion of the findings in the water-mixing experiment

Shekobe (2012) performed similar mixing experiments with water from the same two streams. However, the results that were achieved in that study differs greatly from what was found in the experiments conducted in this study. Shekobe saw a 40 to 90 % reduction in DRP, DUP, Ali and Alo during the 5 h experiments. The observed changes in the water-mixing experiments shown in the present thesis were less obvious: Al concentrations were reduced about 25 % from the conservative mix and parts of the DRP was transformed to DUP. It was expected that the DOM in the forest water would become less soluble due to the higher ionic strength, complexation with $Ca^{2+}$ and co-precipitation with Al, and sorb to the high concentration of TSS in the agricultural water. The observed effect was however rather minuscule. The molecular weight of the TNOM was found to increase, but the 254 nm

absorbency (a proxy for the TOC) in the filtrated water did not decrease indicating no particle formation.

One reason for different results between the current experiments and the previous experiments by Shekobe (2012) is the differences in the water quality of the samples used for experiments. All data from characterization are given in Appendix 8 together with data from Shekobe (2012). Notably, the conductivity is three times higher in the agricultural sample that Shekobe used than the one used here. This reflects higher concentrations of $Cl^-$, $SO_4^{2-}$, $Na^+$, $Mg^{2+}$ and $Ca^{2+}$ – and twice as high P concentrations. The $Ca^{2+}$ concentration is 5 times higher in the previous study, and this might greatly have affected the solubility of DOM. Furthermore, the P concentration was twice as high, and the alkalinity 2.5 times higher in Shekobe's agricultural sample. Furthermore, the pH of the forest stream was 4.5 in the previous study while it was 5.6 in the current study, however this was sought corrected by adjusting the pH. For the forested samples, more than twice as high content of organic carbon was found in Shekobe's sample, and P fractions were also generally higher in this sample. Ala in the forest samples is probably similar within the uncertainties of the measurements. These differences in water quality are probably due to the fact that the samples used in Shekobe's study were collected during low flow conditions while the samples used for the current study were collected during high flow conditions. The chemical differences between the forest water and agricultural water were overall much greater in the previous study than in the present study.

The pH is a very important factor governing Al speciation, DOM solubility and sorption of P to particles (see Chapter 5.5). The high pH (i.e. close to 7) in the water mixes of the current study with low P addition has likely allowed for a greater formation of $Al(OH)_4^-$, which has less capacity to adsorb phosphorous. At pH 7 about 90% of the labile aluminium in solution exists as $Al(OH)_4^-$. pH values during the experiments of Shekobe (2012) are not known, but could be assumed to be close to 6.5 as this was the pH of the agricultural sample. The observed increase in PP in the High P concentration experiment is thus possibly explained by the lower pH in this experiment compared to the three other experiments.

Other properties of the sample water have possibly also affected the results: The higher ionic strength in Shekobe's samples might have caused greater precipitation of the organic matter, leading to lower DUP and possibly co-precipitating DRP. The higher P concentration might have changed equilibriums toward favouring removal of P from solution.

Another reason for differing results between the two studies may be differences in the experimental design. Shekobe (2012) filtered the aliquots immediately, but waited 5 h before measurements. In the present thesis, measurements were done immediately, except for Al analysis. When Alof was measured, the sample was immediately exchanged on the column, but the analysis of monomeric Al was performed later the same day.

Upon mixing, DRP was converted to DUP, which is considered not bioavailable. DUP is determined as the difference between DTP and DRP and is as such the non-labile dissolved P in solution. The formation of non-labile P is conceptually the first step towards the formation of PP when the particles grow larger than 0.45µm. This means that some P can be lost permanently when water from agriculture and forest is mixed.

However, when the particles from the mixing experiment were exposed to the Lake water with low DRP concentrations, the DUP was gradually transformed to DRP again. One third of the radioactive phosphorus stayed particulate even after 16 days, indicating that some of the newly formed DUP might not become available to algae. If this was caused by the formation of new colloids or sorption to particles or organic matter already existing in the water is not certain.

## 5.5 Results from modelling the effect of pH on the sorption of phosphorus to hydrous ferric oxide

Figure 5-24 shows that almost all the phosphate is absorbed by low pH values, but above pH 6 the concentration of dissolved phosphate in the water increased dramatically, and above pH 10 most of the phosphate is dissolved. This is the same effect as is seen in eutrophic lakes: the elevated pH caused by the high photosynthesis during algal blooms causes desorption of $PO_4$(E.g. Ekholm, 1994). pH is thus a positive feedback mechanism for eutrophication.

In Lake Vansjø, a pH above 8.5 have been measured every the summer for the last 5 years (Skarbøvik et al., 2014). In 2009 the pH was at one point close to 10, and pH values above 10 have been previously reported.

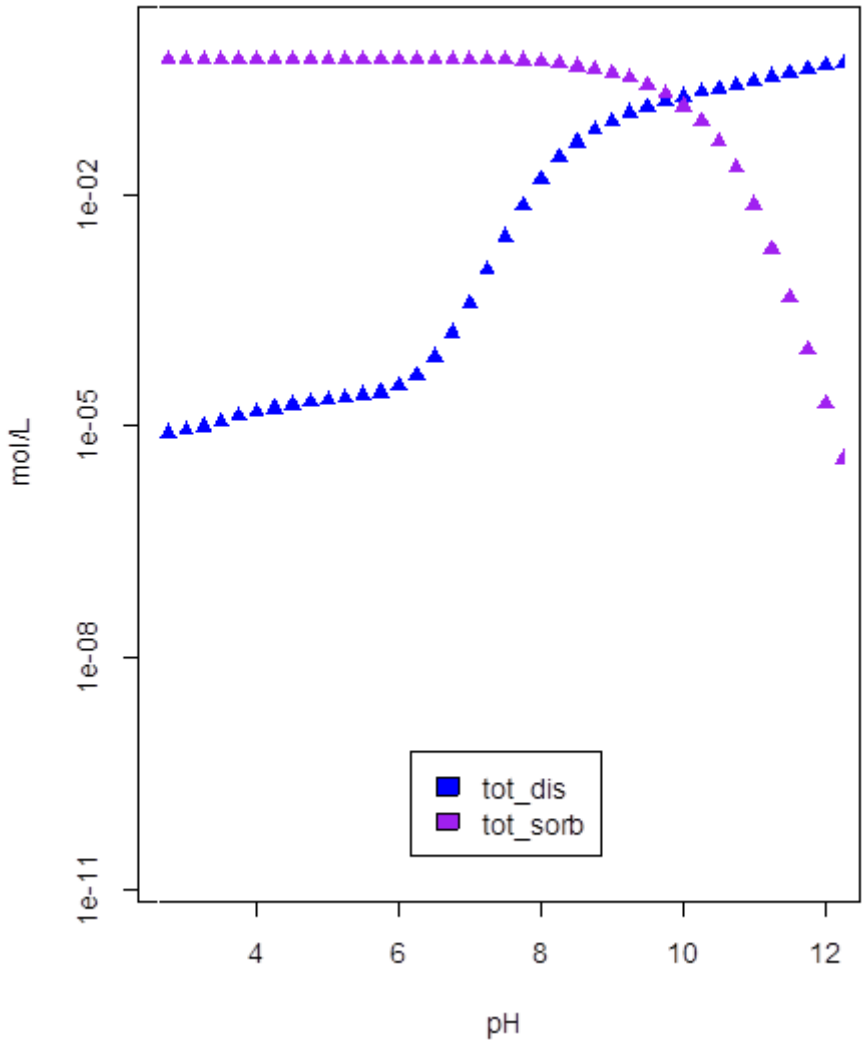


*Figure 5-24: pH dependence of variation of the total dissolved and sorbed phosphate in equilibrium with hydrous ferric oxide.*

# 6 CONCLUSIONS

P has previously been seen to precipitate with Al when agricultural and forested water is mixed (Shekobe, 2012). The results from the water-mixing experiment indicate that pH is a main controlling factor for this precipitation. The elevated pH compared to the forest water causes Al to precipitate, however when the pH is circumneutral, the P was not removed by Al precipitation. The reason for this is thought to be the negative charge of the monomeric Al by higher pH.

The sorption-desorption experiments implies that eroded soil particles more likely will contribute to decrease the concentration of dissolved P in Lake Vansjø than constituting an important source of P for algae growth, despite the large amounts of P that is transported with particles to the Lake.

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# 8 APPENDIX

## 8.1 Results from characterization of water and comparison with samples of Shekobe (2012)

*Table 8-1: Results from Al characterization of water samples, including which filter that was used for filtration before measurement (see footnotes below table for explanation), standard deviation, number of replicates and data from Shekobe (2012) for comparison.*

| | | Agriculture (Støa) | | | Watershed (Hobøl) | | | Forest (Dalen) | | | Lake (Vansjø) | | | Shekobe: | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | Agriculture | Forest | |
| | **Filter** | **Value** | **St.dev.** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **St.dev.** | **Replicates** | **Value** | **St.dev.** | **Replicates** | **Value** | **Value** | **Unit** |
| **Aluminium fractionation** | | | | | | | | | | | | | | | | |
| Ala | | 1,8 | 0,3 | 3 | | | | 8,1 | 0,8 | 2 | 0,6 | | 1 | | 11,60 | µmol/L |
| Alaf | M | 1,7 | 0,6 | 5 | | | | 10,6 | 2,7 | 6 | 1,5 | 0,7 | 3 | | | µmol/L |
| Particulate Ala | | 0,0 | | | | | | 0,0 | | | 0,0 | | | | | µmol/L |
| Alo | | | | | | | | | | | | | | | 7,82 | µmol/L |
| Alof | M | 1,19 | 1,0 | 4 | | | | 9,05 | 1,24 | 4 | 1,44 | 0,26 | 2 | | | µmol/L |
| Ali | | | | | | | | | | | | | | | 3,78 | µmol/L |
| Alif | M | 0,5 | | | | | | 1,6 | | | | | | | | µmol/L |
| Alr | | 9,6 | 3,3 | 5 | | | | 15,6 | 2,7 | 4 | 4,5 | 0,7 | 3 | | | µmol/L |
| Alrf | M | 3,3 | 0,6 | 3 | | | | 13,3 | 0,6 | 2 | 2,8 | | 1 | | | µmol/L |
| Total particulate Al | | 6,3 | | | | | | 2,3 | | | 1,7 | | | | | µmol/L |

*M: HAWP MF-Millipore 0.45 µm Membrane (Cat. No. HAWP04700)*

*Table 8-2: Results from P characterization of water samples, including which filter that was used for filtration before measurement (see footnotes below table for explanation), standard deviation, number of replicates and data from Shekobe (2012) for comparison.*

| | | Agriculture (Støa) | | | Watershed (Hobøl) | | | Forest (Dalen) | | | Lake (Vansjø) | | | Shekobe: | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | Agriculture | Forest | |
| | **Filter** | **Value** | **St.dev.** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **St.dev.** | **Replicates** | **Value** | **St.dev.** | **Replicates** | **Value** | **Value** | **Unit** |
| **P-fractionation 0,45 µm** | | | | | | | | | | | | | | | | |
| TP | - | 5,5 | 0,5 | 6 | 2,8 | 0,4 | 3 | 0,4 | 0,2 | 3 | 0,6 | | 3 | 11,4 | 1,1 | µmol/L |
| DTP | M, CN* | 2,5 | 0,4 | 2 | 2,1 | 0,2 | 4 | 0,4 | 0,04 | 2 | 0,5 | | 2 | 6,6 | 0,9 | µmol/L |
| DRP (not acidified**) | M, CN* | 2,1 | 0,6 | 2 | 1,5 | | 1 | 0,4 | 0,09 | 2 | 0,5 | | 2 | 5,8 | 0,5 | µmol/L |
| DUP | M, CN* | 0,4 | 0,2 | | 0,6 | | | 0,0 | | | 0,1 | | | 0,8 | 0,4 | µmol/L |
| PP | M, CN* | 3,0 | 0,8 | | 0,6 | | | 0,0 | | | 0,0 | | | 4,8 | 0,2 | µmol/L |
| **P-fractionation 0,7 µm** | | | | | | | | | | | | | | | | |
| TP | - | 5,5 | 0,5 | 6 | 2,8 | 0,4 | 3 | 0,4 | 0,2 | 3 | 0,6 | | 3 | | | µmol/L |
| DTP | GF | 4,7 | 0,3 | 2 | 1,7 | | 1 | 0,2 | 0,03 | 2 | 0,3 | | 1 | | | µmol/L |
| DRP (acidified) | GF | 3,7 | 0,1 | 2 | 1,3 | | 1 | 0,2 | 0,02 | 2 | 0,3 | | | | | µmol/L |
| DUP | GF | 1,0 | 0,2 | 2 | 0,4 | | | 0,0 | | | 0,0 | | | | | µmol/L |
| PP | GF | 0,9 | 0,4 | 2 | 1,1 | | | 0,3 | | | 0,2 | | | | | µmol/L |

*GF: GF/F Glass Microfibre Filters from Whatman (Cat. No 1825-047, 0.7 µm)*
*CN: Cellulose Nitrate 0.45 Filter from Sartorius (Cat. no. 13906 47 ACN)*
*M: HAWP MF-Millipore 0.45 µm Membrane (Cat. No. HAWP04700)*
** For the P fractionation with 0.45 µm filter paper, Millipore filter paper was used for the three samples that were used for the water-mixing experiment, while for the sample representing the watershed, used for the sorption-desorption experiment, cellulose nitrate filters were used.*
***DRP samples filtrated with 0.45 µm were not acidified after filtration, except for the Agricultural sample (Hobøl)*

*Table 8-3: Results from characterization of organic matter in water samples, including which filter that was used for filtration before measurement (see footnotes below table for explanation), standard deviation, number of replicates and data from Shekobe (2012) for comparison.*

| | | Agriculture (Støa) | | | Watershed (Hobøl) | | | Forest (Dalen) | | | Lake (Vansjø) | | | Shekobe | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | Agriculture | Forest | |
| | **Filter** | **Value** | **Stdev** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **Value** | **Unit** |
| **Carbon and nitrogen** | | | | | | | | | | | | | | | | |
| DOC ( storage) | S | 8,3 | | 1 | 7,6 | | 1 | 13,3 | | 1 | 7,6 | | 1 | | | mg/L |
| DOC during experiments | S | 7,4 | 0,1 | 4 | 6,9 | 0,1 | 4 | 13,0 | 0,1 | 4 | 7,5 | 0,1 | 4 | | | mg/L |
| TOC | | | | | | | | | | | | | | 7 | 30,95 | mg/L |
| **UV/Vis absorbance** | | | | | | | | | | | | | | | | |
| Abs. 254 nm, unfiltered | - | 0,544 | 0,023 | 5 | 0,697 | | 1 | 0,648 | 0,015 | 6 | 0,327 | 0,002 | 3 | 0,181 | 1,5 | /cm |
| Abs. 400 nm, unfiltered | - | 0,093 | 0,010 | 5 | 0,116 | | 1 | 0,076 | 0,003 | 6 | 0,036 | 0,002 | 3 | 0,015 | 0,17 | /cm |
| Abs. 600 nm, unfiltered | - | 0,013 | 0,005 | 5 | 0,030 | | 1 | 0,007 | 0,002 | 6 | 0,006 | 0,002 | 3 | 0,011 | 0,019 | /cm |
| sUVa unfiltered | - | | | | | | | | | | | | | 2,6 | 4,8 | mg/Lm |
| SAR unfiltered sample | - | 5,8 | | | 6,0 | | | 8,5 | | | 9,2 | | | 12,1 | 8,8 | |
| E4:E6 unfiltered sample | - | 7,2 | | | 3,9 | | | 10,9 | | | 5,6 | | | 1,4 | 8,9 | |
| Abs. 254 nm, filtered | various | 0,428 | 0,064 | 5 | 0,519 | | 1 | 0,628 | 0,015 | 6 | 0,310 | 0,013 | 3 | | | /cm |
| Abs. 400 nm, filtered | various | 0,056 | 0,017 | 5 | 0,052 | | 1 | 0,072 | 0,003 | 6 | 0,028 | 0,002 | 3 | | | /cm |
| Abs. 600 nm, filtered | various | 0,005 | 0,002 | 5 | 0,007 | | 1 | 0,006 | 0,001 | 6 | 0,003 | 0,002 | 3 | | | /cm |
| sUVa filtered | | 5,4 | | | 7,1 | | | 4,8 | | | 4,1 | | | | | mg/Lm |
| SAR filtered | | 7,7 | | | 10,0 | | | 8,8 | | | 11,2 | | | | | |
| E4:E6 filtered | | 11,1 | | | 7,4 | | | 12,3 | | | 11,1 | | | | | |
| Abs. 254 nm, difference | various | 0,116 | | 5 | 0,178 | | 1 | 0,020 | | 6 | 0,018 | | 3 | | | /cm |
| Abs. 400 nm, difference | various | 0,038 | | 5 | 0,064 | | 1 | 0,005 | | 6 | 0,008 | | 3 | | | /cm |
| Abs. 600 nm, difference | various | 0,008 | | 5 | 0,023 | | 1 | 0,001 | | 6 | 0,004 | | 3 | | | /cm |

*S: Supor® polyethersulfone 0.45 µm membrane filters from Pall*

*Table 8-4: Main anions and cations measured in water samples, including which filter that was used for filtration before measurement (see footnotes below table for explanation), standard deviation, number of replicates and data from Shekobe (2012) for comparison.*

| | | Agriculture (Støa) | | | Watershed (Hobøl) | | | Forest (Dalen) | | | Lake (Vansjø) | | | Shekobe | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | Agriculture | Forest | |
| | **Filter** | **Value** | **Stdev** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **Value** | **Unit** |
| **Main anions (IC)** | | | | | | | | | | | | | | | | |
| F | S | 18,1 | 0,2 | 3 | 4,3 | 0,05 | 3 | low | | 3 | 3,4 | 0,02 | 3 | 15 | 5 | µEq/L |
| Cl | S | 198 | 2 | 3 | 406 | 3 | 3 | 120 | 1 | 3 | 315 | 1 | 3 | 635 | 148 | µEq/L |
| Br | S | low | | 3 | low | | 3 | low | | 3 | low | | 3 | | | µEq/L |
| SO4 | S | 100 | 1 | 3 | 137 | 1 | 3 | 41 | 0,2 | 3 | 107 | 0,4 | 3 | 1900 | 50 | µEq/L |
| NO3 | S | 145 | 0,2 | 3 | 106 | 0,3 | 3 | 25 | 0,3 | 3 | 38 | 0,4 | 3 | 192 | 4 | µEq/L |
| HCO3 | S | | | | | | | | | | | | | | | |
| **Main cations (IC)** | | | | | | | | | | | | | | | | |
| Na | S | 136 | 0,3 | 3 | 342 | 0,7 | 3 | 116 | 0,4 | 3 | 295 | 0,6 | 3 | | | µEq/L |
| K | S | 229 | 0,5 | 3 | 76 | 0,1 | 3 | 46 | 0,2 | 3 | 43 | 0,2 | 3 | | | µEq/L |
| Mg | S | 290 | 0,8 | 3 | 138 | 0,7 | 3 | 32 | 0,2 | 3 | 142 | 0,4 | 3 | | | µEq/L |
| Ca | S | 705 | 2 | 3 | 291 | 2 | 3 | 41 | 0,6 | 3 | 279 | 0,9 | 3 | | | µEq/L |
| **Cations (ICP-OES)** | S | | | | | | | | | | | | | | | |
| Na | S | 174 | | 1 | 407 | | | 145 | | | 373 | | | 385 | 186 | µEq/L |
| K | S | 241 | | 1 | 84 | | | 50 | | | 50 | | | 148 | 57 | µEq/L |
| Mg | S | 357 | | 1 | 175 | | | 48 | | | 184 | | | 1260 | 80 | µEq/L |
| Ca | S | 811 | | 1 | 343 | | | 50 | | | 340 | | | 3900 | 118 | µEq/L |
| Fe | | | | | | | | | | | | | | 1,7 | 0,77 | µmol/L |
| Mn | | | | | | | | | | | | | | 1,3 | 0,08 | µmol/L |
| Si | | | | | | | | | | | | | | 6,4 | 2,2 | µmol/L |

*S: Supor® polyethersulfone 0.45 µm membrane filters from Pall*

*Table 8-5: Trace metals measured in water samples, including which filter that was used for filtration before measurement (see footnotes below table for explanation), standard deviation, number of replicates and data from Shekobe (2012) for comparison.*

| | | Agriculture (Støa) | | | Watershed (Hobøl) | | | Forest (Dalen) | | | Lake (Vansjø) | | | Shekobe | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | Agriculture | Forest | |
| | **Filter** | **Value** | **Stdev** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **Stdev** | **Replicates** | **Value** | **Value** | **Unit** |
| **Dissolved trace metals** | | | | | | | | | | | | | | | | |
| Fe | S | 6,2 | | 1 | 2,7 | | 1 | 8,2 | | 1 | 1,9 | | 1 | | | µmol/L |
| Al | S | 0,71 | | 1 | 3,9 | | 1 | 12,3 | | 1 | 2,1 | | 1 | | | µmol/L |
| Cr | S | 0,010 | | 1 | 0,017 | | 1 | 0,012 | | 1 | 0,012 | | 1 | | | µmol/L |
| Mn | S | 0,012 | | 1 | 0,014 | | 1 | 1,1 | | 1 | 0,022 | | 1 | | | µmol/L |
| Cu | S | 0,053 | | 1 | 0,048 | | 1 | 0,012 | | 1 | 0,029 | | 1 | | | µmol/L |
| Zn | S | 0,056 | | 1 | 0,072 | | 1 | 0,14 | | 1 | 0,011 | | 1 | | | µmol/L |
| Cd | S | 8,9E-05 | | 1 | 0,0003 | | 1 | 0,0003 | | 1 | 1,78E-05 | | 1 | | | µmol/L |
| Sn | S | 0,0014 | | 1 | 0,0003 | | 1 | 0,0036 | | 1 | 0,0002 | | 1 | | | µmol/L |
| Pb 206 | S | 0,0011 | | 1 | 0,0006 | | 1 | 0,0026 | | 1 | 0,0002 | | 1 | | | µmol/L |
| Pb 207 | S | 0,0014 | | 1 | 0,0007 | | 1 | 0,0029 | | 1 | 0,0003 | | 1 | | | µmol/L |
| Pb 208 | S | 0,0013 | | 1 | 0,0007 | | 1 | 0,0029 | | 1 | low | | 1 | | | µmol/L |

*S: Supor® polyethersulfone 0.45 µm membrane filters from Pall*

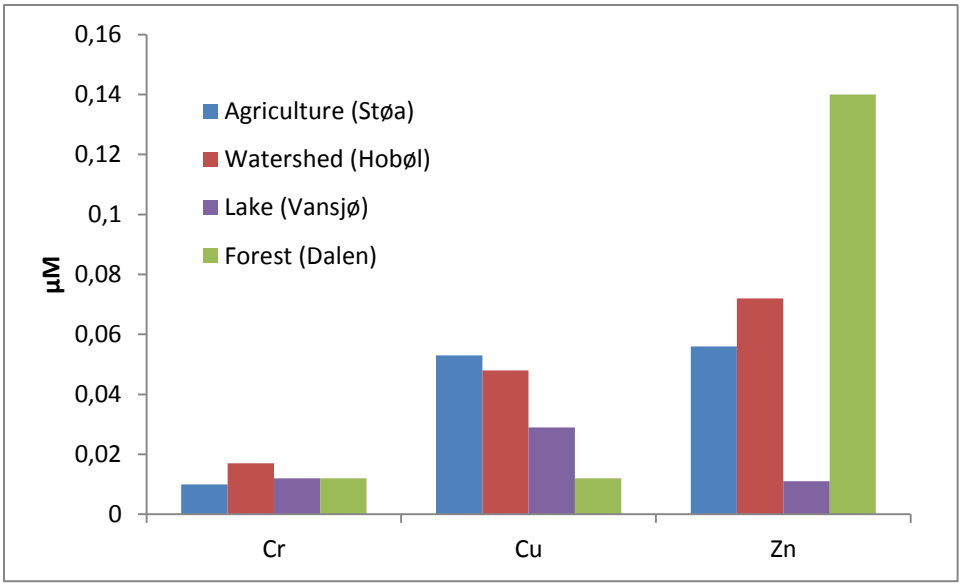


*Figure 8-1: Chromium, copper and zinc in the water samples*

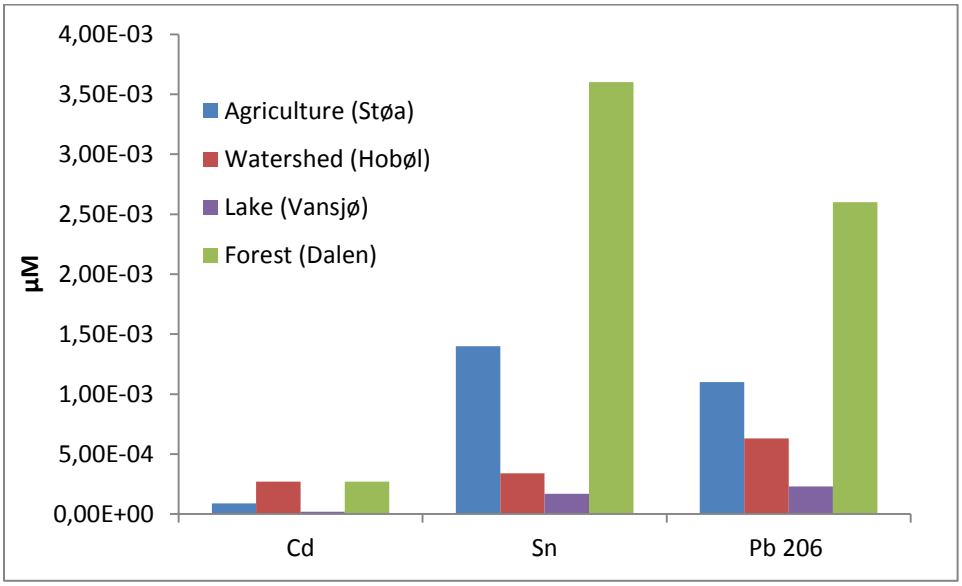


*Figure 8-2: Cadmium, tin and lead in the water samples.*

## 8.2 Results from characterization of particles

*Table 8-6: Results from characterization of particles*

| Parameter | Agricultural (Støa) | Watershed (Hobøl) |
|---|---|---|
| LOI (%) | 5,9 | 5,4 |
| Total phosphorus (mmol P/g) | 0,133 | 0,124 |
| Inorganic phosphorus (mmol P/g) | 0,100 | 0,094 |
| Organic phosphorus (mmol P/g) | 0,032 | 0,029 |

## 8.3 Sorption-desorption experiment

### 8.3.1 R-values and significance from regression

*Table 8-7: R-values from simple linear regression on a logarithmic time scale for time trends for P fractions. Linear regression was performed on data corrected for variations in particle concentration, thus TP is constant and not a part of the analysis, and DTP and PP are mirror images of each other.*

| Experiment | DTP | DRP | PP | DUP |
|---|---|---|---|---|
| High P conc. | 0,89* | 0,73* | -0,89* | -0,06 |
| Low P conc. | 0,61 | 0,53 | -0,61 | 0,00 |
| Blank | -0,51 | -0,42 | 0,51 | -0,57 |
| Effect of filter (CA) | 0,71 | 0,48 | n.m. | -0,21 |
| Effect of filter (GF) | -0,42 | -0,16 | n.m. | 0,05 |

** Slope is significantly different from 0 at a 95 % confidence level.*

### 8.3.2 Correlation between P fractions in sorption-desorption experiment

Table 8-8, Table 8-9, Table 8-10, Table 8-11 and Table 8-12 show the Pearson correlation coefficients (R) between the different P fractions in the sorption-desorption experiments. Data are not corrected for varying particle concentration in aliquots.

*Table 8-8: Pearson correlation coefficient (R) between P fractions in the desorption part of the high concentration sorption-desorption experiment.*

| | TP | DTP | PP | DRP |
|---|---|---|---|---|
| DTP | 0,65 | | | |
| PP | 1,00 | 0,59 | | |
| DRP | 0,62 | 0,86 | 0,57 | |
| DUP | -0,21 | -0,15 | -0,21 | -0,64 |

*Table 8-9: Pearson correlation coefficient (R) between P fractions in the desorption part of the low concentration sorption-desorption experiment.*

| | TP | DTP | PP | DRP |
|---|---|---|---|---|
| DTP | -0,13 | | | |
| PP | 0,99 | -0,29 | | |
| DRP | 0,18 | 0,09 | 0,15 | |
| DUP | -0,23 | 0,62 | -0,32 | -0,72 |

*Table 8-10: Pearson correlation coefficient (R) between P fractions in the desorption part of the blank sorption-desorption experiment.*

| R | TP | DTP | PP | DRP |
|---|---|---|---|---|
| DTP | -0,16 | | | |
| PP | 0,99 | -0,29 | | |
| DRP | -0,42 | -0,84 | 0,83 | |
| DUP | -0,35 | 1,00 | -0,47 | -0,88 |

*Table 8-11: Pearson correlation coefficient (R) between P fractions for the aliquots that were filtered with 0.45 µm cellulose acetate filter paper in the desorption part of the filter comparison sorption-desorption experiment.*

| R | DTP | DRP |
|---|---|---|
| DRP | 0,69 | |
| DUP | -0,31 | -0,90 |

*Table 8-12: Pearson correlation coefficient (R) between P fractions for the aliquots that were filtered with 0.7 µm glass fibre filter paper in the desorption part of the filter comparison sorption-desorption experiment.*

| R | DTP | DRP |
|---|---|---|
| DRP | 0,77 | |
| DUP | 0,18 | -0,50 |

### 8.3.3 Raw data from sorption-desorption experiment

*Figure 8-3: Raw data and calculated concentrations from the Blank sorption-desorption experiment*

| | | Time | TP | DTP | DRP | PP | DUP | Corr. TP | Corr. PP | Particle conc. | TP | DTP | DRP | PP | DUP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | (hours) | µM | µM | µM | µM | µM | µM | µM | g/L | µmol/g particles | | | | |
| Sorption part | **Concentration in water before start** | **0** | 2,8 | 2,1 | 1,5 | 0,6 | 0,6 | | | low | | | | | |
| | **Added P** | | 0,0 | 0,0 | 0,0 | 0,0 | 0,0 | | | 0,1 | 0 | 0 | 0 | 0 | 0 |
| | **Expected concentration of water after adding P** | | 2,8 | 2,1 | 1,5 | 0,6 | 0,6 | | | low | | | | | |
| | **Measured concentration in water after adding P** | | n.m. | n.m. | n.m. | n.m. | n.m. | | | low | | | | | |
| | **Start sorption: particles added** | | n.m. | n.m. | n.m. | n.m. | n.m. | | | 0,1 | | | | | |
| | **End sorption: before sedimentation** | **12** | n.m. | n.m. | n.m. | n.m. | n.m. | | | 0,10 | | | | | |
| | **End sorption: particles sedimented** | **24** | n.m. | n.m. | n.m. | n.m. | n.m. | | | low | | | | | |
| Desorption part | **Concentration in water before start** | **0** | n.m. | n.m. | n.m. | n.m. | n.m. | | | low | | | | | |
| | **Start desorption** | **0,1** | 1,8 | 0,6 | 0,3 | 1,2 | 0,2 | 1,8 | 1,3 | 0,09 | 20 | 6 | 4 | 14 | 3 |
| | **1 h** | **1** | n.m. | n.m. | 0,5 | n.m. | n.m. | 1,8 | | 0,09 | 20 | | 5 | | |
| | **2 h** | **2** | 1,6 | 0,5 | n.m. | 1,1 | n.m. | 1,8 | 1,3 | 0,09 | 20 | 6 | | 14 | |
| | **4 h** | **4** | 1,6 | 0,5 | 0,3 | 1,1 | 0,2 | 1,8 | 1,3 | 0,09 | 20 | 6 | 4 | 15 | 2 |
| | **8 h** | **8** | 1,7 | 0,6 | 0,3 | 1,1 | 0,2 | 1,8 | 1,3 | 0,09 | 20 | 6 | 4 | 14 | 3 |
| | **24 h** | **24** | 2,1 | 0,5 | 0,3 | 1,6 | 0,2 | 1,8 | 1,3 | 0,09 | 20 | 6 | 4 | 14 | 2 |
| | **End desorption** | **51** | 2,1 | n.m. | 0,3 | n.m. | n.m. | 1,8 | | 0,09 | 20 | | 3 | | |

*n.m.: Not measured*

*Figure 8-4: Raw data and calculated concentrations from the Low P concentration sorption-desorption experiment.*

| | | Time | TP | DTP | DRP | PP | DUP | Corr.TP | Corr. PP | Particles | TP | DTP | DRP | PP | DUP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | (hours) | µM | | | | | | | g/L | µmol/g particles | | | | |
| Sorption part | **Concentration in water before start** | | 2,8 | 2,1 | 1,5 | 0,6 | 0,6 | | | low | | | | | |
| | **Added P** | | 1,6 | 1,6 | 1,6 | 0,0 | 0,0 | | | 0,1 | 16 | 16 | 16 | 0 | 0 |
| | **Expected concentration of water after addition of P** | | 4,4 | 3,7 | 3,2 | 0,6 | 0,6 | | | low | | | | | |
| | **Measured concentration in water after addition of P** | | n.m. | n.m. | n.m. | n.m. | n.m. | | | low | | | | | |
| | **Start sorption: particles added** | **0** | n.m. | n.m. | n.m. | n.m. | n.m. | | | 0,1 | | | | | |
| | **Additional P from particles calculated from expected concentration** | | 3,0 | | | | | | | | | | | | |
| | **End sorption: before sedimentation** | **12** | 7,4 | 3,0 | 2,9 | 4,4 | 0,1 | | | 0,10 | 74 | 30 | 29 | 44 | 1 |
| | **End sorption: particles sedimented,** | **24** | 4,5 | 2,8 | 2,5 | 1,7 | 0,2 | | | low | | | | | |
| | **Estimated sorbed amount of P during the sorption part** | | | 1,0 | 0,6 | | 0,3 | | | 0,100 | | 10 | 6 | | 3 |
| | **Estimated original PP** | | | | | 3,0 | | | | 0,100 | | | | 36 | |
| | **Estimated PP at the end of sorption from measured PP in high concentration experiment** | | | | | 4,0 | | | | | | | | | |
| Desorption part | **Concentration in water before start** | **0** | | | | 0,0 | 0,0 | | | low | | | | | |
| | **Starting point estimated from measured PP in high concentration experiment** | | | | | 3,2 | | | 3,2 | 0,081 | | | | 40 | |
| | **Start desorption** | **0,1** | 4,3 | 0,6 | 0,3 | 3,7 | 0,4 | 3,6 | 3,0 | 0,081 | 45 | 8 | 3 | 37 | 4 |
| | **1 h** | **1** | 3,0 | 0,6 | 0,4 | 2,4 | 0,3 | 3,6 | 3,0 | 0,081 | 45 | 8 | 4 | 37 | 4 |
| | **2 h** | **2** | 3,1 | 0,7 | 0,4 | 2,4 | 0,2 | 3,6 | 3,0 | 0,081 | 45 | 8 | 5 | 37 | 3 |
| | **4 h** | **4** | 4,0 | 0,6 | 0,5 | 3,4 | 0,1 | 3,6 | 3,1 | 0,081 | 45 | 7 | 6 | 38 | 1 |
| | **8 h** | **8** | 3,5 | 0,7 | 0,3 | 2,8 | 0,4 | 3,6 | 3,0 | 0,081 | 45 | 8 | 3 | 37 | 5 |
| | **24 h** | **24** | 3,5 | 0,8 | 0,4 | 2,7 | 0,5 | 3,6 | 2,8 | 0,081 | 45 | 10 | 5 | 35 | 6 |
| | **End desorption** | **48** | 3,5 | 0,8 | 0,3 | 2,7 | 0,4 | 3,6 | 2,9 | 0,081 | 45 | 10 | 4 | 35 | 5 |

| | | Time | TP | DTP | DRP | PP | DUP | Corr.TP | Corr. PP | Particles | TP | DTP | DRP | PP | DUP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **102** | 4,3 | 0,8 | 0,5 | 3,5 | 0,2 | 3,6 | 2,9 | 0,081 | 45 | 9 | 7 | 36 | 3 |

*n.m.: Not measured*

*Figure 8-5: Raw data and calculated concentrations from the High P concentration sorption-desorption experiment*

| | | Time | TP | DTP | DRP | PP | DUP | Corr. TP | Corr. PP | Particles | TP | DTP | DRP | PP | DUP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **hours** | µM | | | | | | | **g/L** | **µmol/g particles** | | | | |
| Sorption part | **Concentration in water before start** | | 2,8 | 2,1 | 1,5 | 0,6 | 0,6 | | | low | | | | | |
| | **Added P** | | 3,2 | 3,2 | 3,2 | 0,0 | 0,0 | | | 0,100 | 32 | 32 | 32 | 0 | 0 |
| | **Expected concentration of water after addition of P** | | 6,0 | 5,4 | 4,8 | 0,6 | 0,6 | | | low | | 54 | 48 | | 6 |
| | **Measured concentration in water after addition of P** | | 6,4 | n.m. | 4,2 | n.m. | n.m. | | | low | | | 42 | | |
| | **Start sorption: particles added** | **0** | 8,7 | 4,5 | 4,1 | 4,3 | 0,4 | | | 0,100 | 87 | 45 | 41 | 43 | 4 |
| | **Additional P from particles calculated from expected concentration** | | 2,7 | -0,9 | -0,7 | 3,6 | -0,2 | | | 0,100 | 27 | -9 | -7 | 36 | -2 |
| | **Additional P from particles calculated from measured concentration** | | 2,4 | | -0,1 | | | | | 0,100 | 24 | 0 | -1 | 0 | 0 |
| | **End sorption: before sedimentation** | **12** | n.m. | n.m. | n.m. | n.m. | n.m. | | | 0,100 | | | | | |
| | **End sorption: particles sedimented,** | **24** | 6,4 | 4,3 | 3,9 | 2,1 | 0,4 | | | low | | 43 | 39 | | 4 |
| | **Estimated sorbed amount of P during sorption part** | | | 1,1 | 0,9 | | 0,2 | | | 0,100 | | 11 | 9 | | 2 |
| | **Estimated original PP** | | | | | 3,0 | | | | 0,100 | | | | 30 | |
| | **Estimated PP at the end of sorption part from sums** | | | | | 4,1 | | | | | | | | | |
| Desorption part | **Concentration in water before start** | **0** | n.m. | n.m. | n.m. | n.m. | n.m. | | | low | | | | | |
| | **Theoretical starting point** | | | | | 3,3 | | | | 0,081 | | | | 41 | |
| | **Start desorption** | **0,1** | 3,5 | 0,8 | 0,6 | 2,7 | 0,3 | 3,9 | 3,1 | 0,081 | 49 | 10 | 7 | 38 | 3 |
| | **1 h** | **1** | 3,5 | 0,9 | 0,5 | 2,6 | 0,3 | 3,9 | 3,1 | 0,081 | 49 | 11 | 7 | 38 | 4 |
| | **2 h** | **2** | 3,8 | 0,8 | 0,5 | 2,9 | 0,3 | 3,9 | 3,1 | 0,081 | 49 | 10 | 6 | 38 | 4 |

| | | Time | TP | DTP | DRP | PP | DUP | Corr. TP | Corr. PP | Particles | TP | DTP | DRP | PP | DUP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **4 h** | **4** | 3,2 | 0,9 | 0,5 | 2,4 | 0,3 | 3,9 | 3,1 | 0,081 | 49 | 11 | 7 | 38 | 4 |
| | **8 h** | **8** | 4,0 | 0,8 | 0,6 | 3,2 | 0,3 | 3,9 | 3,1 | 0,081 | 49 | 10 | 7 | 38 | 3 |
| | **24 h** | **24** | 4,2 | 0,9 | 0,7 | 3,3 | 0,2 | 3,9 | 3,0 | 0,081 | 49 | 11 | 8 | 38 | 3 |
| | **48 h** | **48** | 4,0 | 0,9 | 0,6 | 3,0 | 0,3 | 3,9 | 3,0 | 0,081 | 49 | 11 | 8 | 37 | 4 |
| | **75 h** | **75** | 3,9 | 0,9 | 0,7 | 3,0 | 0,3 | 3,9 | 3,0 | 0,081 | 49 | 11 | 8 | 37 | 3 |
| | **100 h** | **100** | 4,5 | 0,9 | 0,6 | 3,6 | 0,3 | 3,9 | 3,0 | 0,081 | 49 | 12 | 8 | 37 | 4 |
| | **End desorption** | **101** | 4,7 | 0,9 | 0,6 | 3,8 | 0,3 | 3,9 | 3,0 | 0,081 | 49 | 11 | 8 | 37 | 4 |

*n.m.: Not measured*

*Figure 8-6: Raw data and calculated concentrations for the filter comparison sorption-desorption experiment, aliquots filtrated with 0.45 µm CA filter paper*.

| | | Time | TP | DTP | DRP | PP | DUP | Particles | DTP | DRP | DUP |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **hours** | µM | µM | µM | µM | µM | **g/L** | **µmol/g particles** | | |
| Sorption part | **Concentration in water before start (0.45 µm AC filter paper)** | | 2,77 | 1,23 | 1,00 | 1,54 | 0,23 | low | | | |
| | **Added P** | | 1,61 | 1,61 | 1,61 | 0,00 | 0,00 | 0,10 | 16,10 | 16,10 | 0,00 |
| | **Expected concentration of water after addition of P** | | 4,38 | 2,84 | 2,61 | 1,54 | 0,23 | low | | | |
| | **Measured concentration in water after addition of P** | | 4,63 | 2,80 | 2,53 | 1,83 | 0,27 | low | | | |
| | **Start sorption: particles added** | **0** | n.m. | 2,71 | 2,57 | n.m. | 0,13 | 0,1 | 27,05 | 25,74 | 1,31 |
| | **End sorption: before sedimentation** | **12** | n.m. | n.m. | n.m. | n.m. | n.m. | 0,10 | | | |
| | **End sorption: particles sedimented, right before decanting of water** | **24** | n.m. | n.m. | n.m. | n.m. | n.m. | low | | | |
| Desorption part | **Concentration in water before start** | **0** | n.m. | 0,37 | 0,16 | n.m. | 0,21 | 0,0837 | 4,46 | 1,95 | 2,51 |
| | **Desorption: 0 h** | **0,1** | n.m. | 0,49 | 0,23 | n.m. | 0,26 | 0,0837 | 5,88 | 2,80 | 3,08 |
| | **1 h** | **1** | n.m. | 0,54 | 0,33 | n.m. | 0,21 | 0,0837 | 6,42 | 3,91 | 2,51 |
| | **2 h** | **2** | n.m. | 0,50 | 0,24 | n.m. | 0,26 | 0,0837 | 5,98 | 2,84 | 3,13 |
| | **4 h** | **4** | n.m. | 0,50 | 0,25 | n.m. | 0,25 | 0,0837 | 6,02 | 3,01 | 3,01 |
| | **8 h** | **8** | n.m. | 0,56 | 0,44 | n.m. | 0,12 | 0,0837 | 6,71 | 5,31 | 1,40 |
| | **24 h** | **24** | n.m. | 0,58 | 0,29 | n.m. | 0,29 | 0,0837 | 6,95 | 3,50 | 3,45 |
| | **Desorption: 48 h** | **48** | n.m. | 0,54 | 0,35 | n.m. | 0,20 | 0,0837 | 6,49 | 4,13 | 2,36 |

*n.m.: Not measured*

*Figure 8-7: Raw data and calculated concentrations for the filter comparison sorption-desorption experiment, aliquots filtrated with 0.7 µM GFfilter.*

| | | Time | TP | DTP | DRP | PP | DUP | Particles | DTP | DRP | DUP |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | hours | µM | µM | µM | µM | µM | g/L | µmol/g particles | | |
| Sorption part | **Concentration in water before start (0.7 µm GF filter)** | | 2,77 | 1,70 | 1,26 | 1,07 | 0,44 | low | | | |
| | **Added P** | | 1,61 | 1,61 | 1,61 | 0,00 | 0,00 | 0,10 | 16,10 | 16,10 | 0,00 |
| | **Expected concentration of water after addition of P** | | 4,38 | 3,31 | 2,87 | 1,07 | 0,44 | low | | | |
| | **Measured concentration in water after addition of P** | | 4,63 | 3,15 | 2,83 | 1,47 | 0,32 | low | | | |
| | **Start sorption: particles added** | **0** | n.m. | 3,16 | 2,93 | n.m. | 0,24 | 0,1 | 31,63 | 29,26 | 2,37 |
| | **End sorption: before sedimentation** | **12** | n.m. | n.m. | n.m. | n.m. | n.m. | 0,10 | | | |
| | **End sorption: particles sedimented, right before decanting of water** | **24** | n.m. | n.m. | n.m. | n.m. | n.m. | low | | | |
| Desorption part | **Concentration in water before start** | **0,01** | n.m. | n.m. | n.m. | n.m. | 0,00 | low | | | |
| | **Desorption: 0 h** | **0,1** | n.m. | 0,67 | 0,38 | n.m. | 0,29 | 0,0837 | 8,02 | 4,53 | 3,49 |
| | **1 h** | **1** | n.m. | 0,71 | 0,40 | n.m. | 0,31 | 0,0837 | 8,49 | 4,77 | 3,72 |
| | **2 h** | **2** | n.m. | 0,71 | 0,40 | n.m. | 0,31 | 0,0837 | 8,52 | 4,80 | 3,72 |
| | **4 h** | **4** | n.m. | 0,69 | 0,40 | n.m. | 0,29 | 0,0837 | 8,28 | 4,82 | 3,45 |
| | **8 h** | **8** | n.m. | 0,66 | 0,40 | n.m. | 0,26 | 0,0837 | 7,88 | 4,76 | 3,13 |
| | **24 h** | **24** | n.m. | 0,64 | 0,32 | n.m. | 0,32 | 0,0837 | 7,64 | 3,79 | 3,85 |
| | **Desorption: 48 h** | **48** | n.m. | n.m. | 0,41 | n.m. | n.m. | 0,0837 | | 4,86 | |

*n.m.: Not measured*

*Figure 8-8: Raw data and calculated concentrations for the sorption-desorption experiment performed with standard clay kaolinite and deionized water.*

| | | Time for graph | TP | TDP | DRP | PP | DOP |
|---|---|---|---|---|---|---|---|
| | | | µM | µM | µM | µM | µM |
| Sorption part | **Previous characterization of water** | | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| | **Added P** | | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| | **Expected concentration of water after addition of P** | | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| | **Measured concentration in water after addition of P** | | n.m. | n.m. | n.m. | n.m. | n.m. |
| | **Start sorption: particles added** | | n.m. | n.m. | n.m. | n.m. | n.m. |
| | **End sorption: before sedimentation** | | n.m. | n.m. | n.m. | n.m. | n.m. |
| | **End sorption: particles sedimented** | | 4,02 | 0,09 | 0,00 | 3,93 | 0,09 |
| Desorption part | **Concentration in water before addition of particles** | **0** | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| | **Start desorption** | **0** | 4,43 | 0,09 | 0,04 | 4,34 | 0,05 |
| | **1 h** | **1** | 4,76 | 0,00 | 0,00 | 4,76 | 0,00 |
| | **2 h** | **2** | 4,49 | 0,00 | 0,00 | 4,49 | 0,00 |
| | **4 h** | **4** | 4,63 | 0,11 | 0,00 | 4,52 | 0,11 |
| | **8 h** | **8** | 4,46 | 0,11 | n.m. | 4,35 | n.m. |
| | **24 h** | **30** | 4,70 | 0,08 | 0,00 | 4,63 | 0,08 |
| | **End desorption** | **51** | 5,03 | 0,08 | 0,00 | 4,96 | 0,08 |

*n.m.: Not measured*

*Figure 8-9: Raw data and calculated concentrations for the sorption-desorption experiment performed with standard clay illite and deionized water.*

| | | Time for graph | TP | TDP | DRP | PP | DOP |
|---|---|---|---|---|---|---|---|
| | | | µM | µM | µM | µM | µM |
| Sorption part | **Previous characterization of water** | | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| | **Added P** | | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| | **Expected concentration of water after addition of P** | | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| | **Measured concentration in water after addition of P** | | n.m. | n.m. | n.m. | n.m. | n.m. |
| | **Start sorption: particles added** | | n.m. | n.m. | n.m. | n.m. | n.m. |
| | **End sorption: before sedimentation** | | n.m. | n.m. | n.m. | n.m. | n.m. |
| | **End sorption: particles sedimented, right before decanting of water** | | 2,24 | 0,80 | 0,79 | 1,44 | 0,01 |
| Desorption part | **Concentration in water before addition of particles** | **0** | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| | **Start desorption** | **0** | 1,05 | 0,17 | 0,10 | 0,89 | 0,06 |
| | **1 h** | **1** | 1,07 | 0,18 | 0,10 | 0,89 | 0,08 |
| | **2 h** | **2** | 1,01 | 0,18 | 0,10 | 0,83 | 0,08 |
| | **4 h** | **4** | n.m. | n.m. | n.m. | n.m. | n.m. |
| | **8 h** | **8** | n.m. | n.m. | n.m. | n.m. | n.m. |
| | **24 h** | **24** | 1,02 | 0,18 | 0,16 | 0,84 | 0,02 |
| | **End desorption** | **48** | 1,05 | 0,20 | 0,11 | 0,86 | 0,08 |

*n.m.: Not measured*

## 8.4 Water-mixing experiment

### 8.4.1 Pearson's R for investigations of time trends

#### 8.4.1.1 Mixing part

*Table 8-13: Pearson's R from linear regression on logarithmic time scale from the mixing part of the water-mixing experiment. The regression does not include the concentrations calculated for the conservative mix. n is number of samples. The degrees of freedom for the regression is n – 2.*

| | Blank | n | Low P I | n | Low P II | n | High P | n |
|---|---|---|---|---|---|---|---|---|
| TP | 0,13 | 4 | -0,21 | 12 | 0,28 | 18 | -0,68 | 5 |
| PP | 0,01 | 4 | -0,16 | 10 | 0,23 | 17 | -0,47 | 5 |
| DTP | 0,84 | 4 | -0,15 | 10 | -0,23 | 17 | -0,75 | 5 |
| DRP | -0,84 | 4 | -0,01 | 10 | -0,09 | 17 | -0,57 | 5 |
| DUP | 0,84 | 4 | -0,19 | 10 | -0,37 | 17 | -0,65 | 5 |
| T32P | -0,05 | 4 | -0,41 | 10 | 0,38 | 17 | - | - |
| P32P | $0,93^{+}$ | 4 | $0,85^{**}$ | 10 | $0,57^{*}$ | 17 | - | - |
| D32P | $-0,99^{**}$ | 4 | $-0,81^{**}$ | 10 | $-0,50^{*}$ | 17 | - | - |
| Alr | - | 2 | - | 2 | $0,48^{*}$ | 18 | - | - |
| Alrf | - | - | - | - | $-0,48^{+}$ | 17 | - | - |
| Alr-Alrf | - | - | - | - | $-0,48^{**}$ | 17 | - | - |
| Ala | - | - | - | - | $-0,44^{+}$ | 18 | - | - |
| Alaf | -0,80 | 4 | $-0,66^{*}$ | 10 | -0,14 | 18 | $-0,84^{+}$ | 5 |
| Ala-Alaf | - | - | - | - | -0,17 | 17 | - | - |
| Alof | $-0,99^{*}$ | 4 | - | 2 | - | - | -0,76 | 4 |
| Alif | 0,77 | 4 | - | 2 | - | - | -0,87 | 4 |
| TNOM254 | -0,82 | 4 | 0,08 | 12 | $0,82^{***}$ | 18 | $0,86^{+}$ | 5 |
| TNOM400 | $1,00^{**}$ | 4 | $0,75^{**}$ | 12 | $0,95^{***}$ | 18 | 0,46 | 5 |
| TNOMSAR | $-0,98^{*}$ | 4 | $-0,73^{**}$ | 12 | $-0,93^{***}$ | 18 | 0,01 | 5 |
| DNOM254 | -0,81 | 4 | -0,43 | 10 | 0,37 | 17 | 0,38 | 5 |
| DNOM400 | $0,97^{*}$ | 4 | 0,06 | 10 | $0,49^{*}$ | 17 | 0,51 | 5 |
| DNOMSAR | $-0,96^{*}$ | 4 | $-0,68^{*}$ | 10 | $-0,57^{*}$ | 17 | -0,50 | 6 |
| PNOM254 | -0,71 | 4 | 0,47 | 10 | -0,13 | 17 | -0,49 | 4 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| PNOM400 | 0,94$^{+}$ | 4 | 0,63$^{*}$ | 10 | 0,34 | 17 | -0,15 | 5 |
| PNOMSAR | -0,89 | 4 | 0,05 | 10 | -0,66$^{**}$ | 17 | -0,42 | 4 |
| pH | 0,70 | 4 | 0,57$^{+}$ | 12 | 0,86$^{***}$ | 18 | 0,71 | 5 |

*+: p < 0.1*
**: p < 0.05*
***: p < 0.01*
****: p < 0.001*

### 8.4.1.2 Desorption part

*Table 8-14: Pearson's R from linear regression on logarithmic time scale from the desorption part of the water-mixing experiment. The regression does not include the concentrations in the lake water. n is number of samples. The degrees of freedom for the regression is n – 2.*

| | Blank (Difference between the two points) | N | Low P I | n | Low P II | N |
|---|---|---|---|---|---|---|
| TP | up | 2 | 0,85** | 9 | 0,83* | 7 |
| PP | up | 2 | 0,68* | 9 | 0,95*** | 7 |
| DTP | no change | 2 | 0,46 | 9 | -0,10 | 15 |
| DRP | up | 2 | 0,85** | 8 | 0,78*** | 15 |
| DUP | up | 2 | -0,83* | 8 | -0,78** | 13 |
| Alr | - | 1 | 0,83 | 3 | 0,92* | 6 |
| Alrf | - | - | - | - | 0,65 | 6 |
| Alr-Alrf | - | - | - | - | 0,73 | 6 |
| Ala | - | - | - | - | 0,12 | 16 |
| Alaf | no change | 2 | 0,45 | 9 | 0,42 | 16 |
| Ala-Alaf | - | - | - | | -0,42 | 16 |
| Alof | down | 2 | 0,20 | 9 | - | - |
| Alif | (up) | 2 | 0,43 | 9 | - | - |
| TNOM254 | up | 2 | 0,78* | 9 | 0,84*** | 15 |
| TNOM400 | up | 2 | 0,80** | 9 | 0,92*** | 15 |
| TNOMSAR | down | 2 | -0,75* | 9 | -0,90*** | 15 |
| DNOM254 | no change | 2 | 0,86** | 9 | 0,75** | 15 |
| DNOM400 | no change | 2 | 0,78* | 9 | 0,79*** | 15 |
| DNOMSAR | no change | 2 | -0,63$^{+}$ | 9 | -0,45$^{+}$ | 15 |
| PNOM254 | up | 2 | 0,10 | 9 | 0,65** | 15 |
| PNOM400 | up | 2 | 0,41 | 9 | 0,88*** | 15 |
| PNOMSAR | down | 2 | -0,21 | 9 | -0,32 | 15 |
| pH | (down) | 2 | 0,70* | 9 | 0,39 | 17 |
| Conductivity | (up) | 2 | -0,66$^{+}$ | 9 | 0,85*** | 17 |

$^{+}$*: p < 0.1*
**: p < 0.05*
***: p < 0.01*
****: p < 0.001*

### 8.4.2 Raw data from the water-mixing experiment

Table 8-15 and Table 8-16 shows raw data for the Blank water-mixing experiment, Table 8-17 and Table 8-18 for the Low P concentration I experiment, Table 8-19 and Table 8-20 for the Low P concentration experiment II and Table 8-21 and Table 8-22 for the High P concentration experiment.

*Table 8-15: Raw data for fractionation of phosphorus, radioactive phosphorus and aluminium in the Blank water-mixing experiment.*

| | | Phosphorus | | | | | Radioactive phosphate | | | Aluminium | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Time** | **TP** | **TDP** | **DRP** | **DOP** | **PP** | **Filtrate** | **Filter residue** | **Total (calculated)** | **Alaf** | **Alof** | **Alif** | **Alr** |
| | **(hours)** | **µM P/L** | | | | | **DPM** | **DPM** | **DPM** | **µM Al/L** | | | |
| **Starting conditions** | Agriculture | 6,5 | 4,5 | 3,6 | 0,8 | 2,0 | | | | 3,5 | 2,7 | 0,9 | 14 |
| | Forest | 0,3 | 0,2 | 0,2 | 0,0 | 0,1 | | | | 11,4 | 9,4 | 1,9 | 19 |
| | Agriculture added 32P | 6,8 | 4,2 | 3,5 | 0,7 | 2,6 | 171527 | 2214 | 173741 | | | | |
| | Conservative mix | 3,5 | 2,2 | 1,8 | 0,3 | 1,3 | 85764 | 1107 | 86870 | 7,4 | 6,0 | 1,4 | 17 |
| **Mixing part** | 0,05 | 3,1 | 2,2 | 1,8 | 0,4 | 0,9 | 86695 | 5929 | 92624 | 7,7 | 5,0 | 2,7 | 14 |
| | 0,9 | 3,2 | 2,2 | 1,8 | 0,4 | 1,0 | 82973 | 8151 | 91124 | 8,0 | 4,4 | 3,6 | |
| | 1,6 | 3,5 | 2,2 | 1,8 | 0,4 | 1,3 | 80972 | 8273 | 89245 | 7,6 | 4,0 | 3,7 | |
| | 48 | 3,2 | 2,3 | 1,7 | 0,6 | 0,9 | 74761 | 17667 | 92428 | 6,8 | 3,2 | 3,6 | 16 |
| | Lake | 0,5 | 0,3 | 0,3 | 0,0 | 0,2 | | | | 2,1 | 1,6 | 0,5 | 5 |
| **Desorption part** | 0,2 | 0,5 | 0,3 | 0,3 | 0,0 | 0,3 | 335 | 140 | 475 | 2,4 | 1,8 | 0,6 | |
| | 1,0 | 0,8 | 0,3 | 0,3 | 0,0 | 0,5 | 961 | 1428 | 2389 | 2,4 | 1,7 | 0,6 | 5 |

*Table 8-16: Raw data for fractionation of pH, conductivity and absorbance in the Blank water-mixing experiment.*

| | | | | TNOM | | | | DNOM | | | | PNOM | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Time (hours)** | **conductivity µS/cm** | **pH** | **Abs254 /cm** | **Abs400 /cm** | **Abs600** | **SAR** | **Abs254 /cm** | **Abs400 /cm** | **Abs600** | **SAR** | **△Abs254 /cm** | **△Abs400 /cm** | **△Abs600 /cm** | **SAR** |
| **Starting conditions** | Agriculture | 116 | 6,8 | 0,548 | 0,085 | 0,012 | 6,4 | 0,484 | 0,065 | 0,007 | 7,4 | 0,064 | 0,020 | 0,005 | 3,2 |
| | Forest | 54 | 5,5 | 0,673 | 0,075 | 0,006 | 9,0 | 0,654 | 0,071 | 0,005 | 9,2 | 0,019 | 0,004 | 0,001 | 4,8 |
| | Agriculture added 32P | 117 | 7,1 | | | | | | | | | | | | |
| | Conservative mix | 85 | 5,8 | 0,611 | 0,080 | 0,009 | 7,7 | 0,569 | 0,068 | 0,006 | 8,3 | 0,042 | 0,012 | 0,003 | 3,5 |
| **Mixing part** | 0,05 | 79 | 6,9 | 0,625 | 0,088 | 0,013 | 7,1 | 0,573 | 0,071 | 0,006 | 8,1 | 0,052 | 0,017 | 0,007 | 3,1 |
| | 0,9 | 78 | 6,8 | 0,625 | 0,091 | 0,013 | 6,9 | 0,575 | 0,072 | 0,006 | 8,0 | 0,050 | 0,019 | 0,007 | 2,6 |
| | 1,6 | 78 | 7,1 | 0,626 | 0,091 | 0,013 | 6,9 | 0,573 | 0,073 | 0,006 | 7,8 | 0,053 | 0,018 | 0,007 | 2,9 |
| | 48 | 108 | 7,1 | 0,608 | 0,095 | 0,014 | 6,4 | 0,56 | 0,074 | 0,006 | 7,6 | 0,048 | 0,021 | 0,008 | 2,3 |
| | Lake | 106 | 6,9 | 0,327 | 0,033 | 0,004 | 9,9 | 0,305 | 0,026 | 0,001 | 11,7 | 0,022 | 0,007 | 0,003 | 3,1 |
| **Desorption part** | 0,2 | 105 | 6,8 | 0,326 | 0,036 | 0,006 | 9,1 | 0,307 | 0,026 | 0,001 | 11,8 | 0,019 | 0,010 | | 1,9 |
| | 1,0 | 106 | 6,7 | 0,349 | 0,053 | 0,016 | 6,6 | 0,307 | 0,027 | 0,001 | 11,4 | 0,042 | 0,026 | 0,015 | 1,6 |

*Table 8-17: Raw data for fractionation of phosphorus, radioactive phosphorus and aluminium in the Low P concentration I water-mixing experiment.*

| | | Phosphate | | | | | Radioactive phosphate | | | Aluminium | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time | TP | TDP | DRP | DOP | PP | Filtrate | Filter residue | Total (calculated) | Alaf | Alof | Alif | Alr |
| | hours | µmol P/L | | | | | DPM | DPM | DPM | µmol Al/L | | | |
| Starting conditions | Agriculture | 5,3 | 2,8 | 2,4 | 0,4 | 2,5 | | | | 2,7 | 1,1 | 1,6 | 9 |
| | Forest | 0,4 | 0,4 | 0,3 | 0,1 | 0,0 | | | | 11,2 | 8,4 | 2,8 | 16 |
| | Agriculture added 32P | 5,2 | 2,9 | 2,4 | 0,5 | 2,3 | 170453 | 7732 | 178185 | | | | |
| | Forest added Al | 0,4 | 0,3 | 0,1 | 0,3 | 0,0 | | | | 24,5 | 15,8 | 8,8 | 35 |
| | Conservative mix | 3,0 | 1,7 | 1,3 | 0,4 | 1,3 | 92137 | 4179 | 96316 | 12,7 | 7,9 | 4,9 | 21 |
| Mixing part | 0,03 | 3,2 | | | | | | | | | | | 19 |
| | 0,60 | 3,3 | 2,3 | 1,5 | 0,8 | 1,0 | 84286 | 12730 | 97016 | 9,4 | | | |
| | 0,83 | 3,2 | 2,6 | 1,9 | 0,6 | 0,6 | 86406 | 11300 | 97706 | 9,6 | 7,8 | 1,8 | |
| | 1,27 | 3,2 | 2,2 | 1,6 | 0,6 | 1,0 | 82356 | 14905 | 97260 | 9,9 | | | |
| | 1,47 | 3,2 | 2,2 | 1,7 | 0,5 | 1,0 | 82707 | 14463 | 97170 | 9,5 | | | |
| | 1,60 | 3,2 | 2,4 | 1,7 | 0,6 | 0,8 | 85061 | 12398 | 97459 | 9,3 | | | |
| | 1,78 | 3,3 | 2,3 | 1,6 | 0,7 | 0,9 | 82304 | 14946 | 97250 | 9,3 | | | |
| | 2,02 | 3,4 | 2,4 | 1,7 | 0,7 | 1,0 | 85840 | 12397 | 98238 | 9,6 | | | |
| | 2,25 | 3,2 | 2,2 | 1,6 | 0,6 | 1,0 | 83072 | 14294 | 97366 | 9,4 | | | |
| | 5,02 | 3,2 | | | | | | | | | | | |
| | 5,43 | 3,1 | 2,1 | 1,7 | 0,4 | 1,0 | 77911 | 18537 | 96448 | 9,4 | | | |
| | 25 | 3,1 | 2,4 | 1,7 | 0,7 | 0,7 | 77738 | 19139 | 96878 | 9,0 | 4,8 | 4,2 | 29 |
| | Lake | 0,6 | 0,5 | 0,5 | 0,1 | 0,0 | 0 | 0 | 0 | 1,7 | 1,3 | 0,4 | 5 |
| Desorption part | 0,02 | 0,6 | 0,6 | 0,4 | 0,2 | 0,0 | 490 | 322 | 812 | 1,7 | 1,3 | 0,4 | 3 |
| | 0,25 | 0,6 | 0,7 | 0,4 | 0,3 | 0,0 | 599 | 397 | 995 | 1,7 | 1,1 | 0,5 | |
| | 0,47 | 0,7 | 0,6 | 0,4 | 0,2 | 0,1 | 688 | 463 | 1150 | 1,7 | 1,2 | 0,5 | |
| | 0,72 | 0,6 | 0,6 | 0,4 | 0,2 | 0,0 | 772 | 606 | 1378 | 1,9 | 1,2 | 0,7 | |
| | 0,98 | 0,7 | 0,7 | 0,5 | 0,2 | 0,0 | 820 | 647 | 1467 | 1,6 | 1,2 | 0,4 | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2,05 | 0,8 | 0,7 | | | 0,1 | 1142 | 1035 | 2177 | 1,6 | 1,2 | 0,4 | |
| | 2,52 | 0,7 | 0,6 | 0,5 | 0,1 | 0,1 | 1295 | 1232 | 2527 | 1,6 | 1,1 | 0,5 | |
| | 21 | 0,8 | 0,8 | 0,8 | 0,0 | 0,1 | 3465 | 1303 | 4769 | 1,9 | 1,4 | 0,5 | 6 |
| | 21 | 0,8 | 0,7 | 0,6 | 0,1 | 0,1 | 3406 | 1372 | 4778 | 1,8 | 1,2 | 0,6 | 4 |
| | 44 | | | | | | 3756 | 740 | 4495 | | | | |

*Table 8-18: Raw data for fractionation of pH, conductivity and absorbance in the Low P concentration I water-mixing experiment.*

| | | | | TNOM | | | | DNOM | | | | PNOM | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Time hours** | **conductivity µS/cm** | **pH** | **Abs254** | **Abs400** | **Abs600** | **SAR** | **Abs254** | **Abs400** | **Abs600** | **SAR** | **△Abs254** | **△Abs400** | **SAR** |
| **Starting conditions** | Agriculture | 129 | 6,9 | 0,531 | 0,090 | 0,015 | 5,9 | 0,380 | 0,042 | 0,004 | 9,0 | 0,151 | 0,048 | 3,1 |
| | Forest | 48 | 5,8 | 0,649 | 0,079 | 0,010 | 8,2 | 0,621 | 0,072 | 0,008 | 8,6 | 0,028 | 0,007 | 4,0 |
| | Agriculture added 32P | 141 | 6,7 | | | | | | | | | | | |
| | Forest added Al | 88 | 4,6 | 0,632 | 0,075 | 0,009 | 8,4 | 0,605 | 0,069 | 0,006 | 8,8 | 0,028 | 0,006 | 4,6 |
| | Conservative mix | 117 | 4,8 | 0,577 | 0,083 | 0,012 | 6,9 | 0,483 | 0,054 | 0,005 | 8,9 | 0,094 | 0,029 | 3,3 |
| **Mixing part** | 0,03 | 112 | 6,2 | 0,578 | 0,080 | 0,011 | 7,2 | | | 0,004 | | | | |
| | 0,60 | 111 | 6,4 | 0,575 | 0,079 | 0,011 | 7,3 | 0,522 | 0,062 | 0,005 | 8,4 | 0,054 | 0,017 | 3,1 |
| | 0,83 | 110 | 6,7 | 0,583 | 0,081 | 0,011 | 7,2 | 0,550 | 0,065 | 0,006 | 8,5 | 0,034 | 0,016 | 2,1 |
| | 1,27 | 112 | 6,6 | 0,593 | 0,082 | 0,012 | 7,2 | 0,525 | 0,063 | 0,005 | 8,3 | 0,069 | 0,019 | 3,6 |
| | 1,47 | 112 | 6,6 | 0,585 | 0,083 | 0,011 | 7,0 | 0,531 | 0,063 | 0,005 | 8,4 | 0,055 | 0,020 | 2,7 |
| | 1,60 | 113 | 6,7 | 0,590 | 0,081 | 0,011 | 7,3 | 0,535 | 0,065 | 0,006 | 8,2 | 0,056 | 0,016 | 3,5 |
| | 1,78 | 113 | 6,8 | 0,587 | 0,084 | 0,012 | 7,0 | 0,526 | 0,063 | 0,006 | 8,3 | 0,062 | 0,021 | 2,9 |
| | 2,02 | 113 | 6,9 | 0,587 | 0,084 | 0,012 | 7,0 | 0,538 | 0,066 | 0,006 | 8,1 | 0,050 | 0,018 | 2,8 |
| | 2,25 | | 7,0 | 0,588 | 0,084 | 0,012 | 7,0 | 0,529 | 0,064 | 0,005 | 8,3 | 0,060 | 0,020 | 3,0 |
| | 5,02 | 136 | 6,8 | 0,571 | 0,082 | | 7,0 | | | | | | | |
| | 5,43 | 133 | 7,2 | 0,575 | 0,084 | 0,012 | 6,8 | 0,504 | 0,060 | 0,005 | 8,4 | 0,071 | 0,024 | 3,0 |
| | 25 | 133 | 6,5 | 0,585 | 0,086 | 0,015 | 6,8 | 0,523 | 0,065 | 0,005 | 8,0 | 0,062 | 0,021 | 3,0 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Lake | 87 | 6,6 | 0,330 | 0,037 | 0,008 | 8,9 | 0,325 | 0,030 | 0,005 | 10,8 | 0,005 | 0,007 | 0,7 |
| **Desorption part** | 0,02 | 109 | 6,6 | 0,332 | 0,036 | 0,007 | 9,2 | 0,310 | 0,029 | 0,003 | 10,7 | 0,022 | 0,007 | 3,1 |
| | 0,25 | 108 | 6,8 | 0,330 | 0,037 | 0,007 | 8,9 | 0,321 | 0,031 | 0,003 | 10,4 | 0,009 | 0,006 | 1,5 |
| | 0,47 | 108 | 6,8 | 0,332 | 0,037 | 0,007 | 9,0 | 0,321 | 0,031 | 0,002 | 10,4 | 0,011 | 0,006 | 1,8 |
| | 0,72 | 109 | 6,7 | 0,331 | 0,035 | 0,006 | 9,5 | 0,321 | 0,032 | 0,002 | 10,0 | 0,010 | 0,003 | 3,3 |
| | 0,98 | 109 | 7,0 | 0,332 | 0,038 | 0,005 | 8,7 | 0,322 | 0,030 | 0,001 | 10,7 | 0,010 | 0,008 | 1,3 |
| | 2,05 | 113 | 7,0 | 0,334 | 0,040 | 0,006 | 8,4 | 0,323 | 0,033 | 0,002 | 9,8 | 0,011 | 0,007 | 1,6 |
| | 2,52 | 113 | 6,7 | 0,333 | 0,037 | 0,006 | 9,0 | 0,319 | 0,033 | 0,004 | 9,7 | 0,014 | 0,004 | 3,5 |
| | 21 | 89 | 6,9 | 0,344 | 0,042 | 0,010 | 8,2 | 0,327 | 0,033 | 0,004 | 9,9 | 0,017 | 0,009 | 1,9 |
| | 21 | 88 | 7,0 | 0,346 | 0,042 | 0,008 | 8,2 | 0,324 | 0,032 | 0,004 | 10,1 | 0,022 | 0,010 | 2,2 |
| | 44 | | | | | | | | | | | | | |

*Table 8-19: Raw data for fractionation of phosphorus, radioactive phosphorus and aluminium in the Low P concentration II water-mixing experiment.*

| | | Phosphate | | | | | Radioactive phosphate | | | Aluminium | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time<br>hours | TP<br>µmol P/L | TDP<br>µmol P/L | DRP<br>µmol P/L | DOP<br>µmol P/L | PP<br>µmol P/L | Filtrate<br>DPM | Filter residue<br>DPM | Total (calculated)<br>DPM | Ala | Alaf | Ala-Alaf | Alr | Alrf | Alr-Alrf |
| | | | | | | | | | | µmol Al/L | | | | | |
| Starting conditions | Agriculture | 5,8 | 2,2 | 1,7 | 0,6 | 3,6 | | | | 1,6 | 1,4 | 0,1 | 10 | 3 | 7 |
| | Forest | 0,6 | 0,4 | 0,5 | 0,0 | 0,3 | | | | 8,6 | 8,0 | 0,6 | 14 | 13 | 1 |
| | Agriculture added 32P | 6,0 | 3,5 | 2,7 | 0,8 | 2,5 | 166921 | 10436 | 177357 | 1,6 | 1,6 | 0,0 | 10 | 3 | 8 |
| | Forest added Al | 0,6 | 0,3 | 0,4 | 0,0 | 0,3 | | | | 19 | 19 | 0,4 | 27 | 25 | 3 |
| | Conservative mix | 3,3 | 1,9 | 1,6 | 0,3 | 1,4 | 83460 | 5217,8 | 88678 | 10 | 10 | 0,2 | 19 | 14 | 5 |
| Mixing Part | 0,03 | 3,2 | 2,9 | 2,1 | 0,8 | 0,4 | 80381 | 8268 | 88649 | 8,3 | 7,8 | 0,5 | 16 | 16 | 0 |
| | 0,15 | 3,2 | 2,1 | 1,4 | 0,7 | 1,2 | 74007 | 18240 | 92247 | 7,6 | 7,4 | 0,2 | 16 | 13 | 3 |
| | 0,27 | 3,2 | 2,4 | 1,4 | 1,0 | 0,8 | 75006 | 14576 | 89582 | 8,2 | 6,5 | 1,7 | 15 | 13 | 2 |
| | 0,38 | 3,2 | 2,2 | 1,5 | 0,7 | 1,0 | 74847 | 14979 | 89827 | 7,8 | 6,8 | 1,0 | 16 | 13 | 3 |
| | 0,65 | 3,3 | 2,1 | 1,4 | 0,7 | 1,1 | 72752 | 17474 | 90225 | 7,8 | 6,2 | 1,5 | 16 | 13 | 3 |
| | 0,85 | 3,2 | 2,1 | 1,4 | 0,7 | 1,2 | 72266 | 18508 | 90774 | 7,3 | 6,6 | 0,7 | 16 | 12 | 3 |
| | 1,00 | 3,2 | 2,2 | 1,5 | 0,7 | 1,1 | 72969 | 17588 | 90556 | 7,3 | 6,5 | 0,8 | 15 | 13 | 3 |
| | 1,60 | 3,2 | 2,2 | 1,5 | 0,6 | 1,0 | 74429 | 16870 | 91299 | 7,2 | 6,6 | 0,6 | 15 | 13 | 2 |
| | 2,07 | 3,2 | 2,1 | 1,4 | 0,7 | 1,1 | 72919 | 17128 | 90047 | 7,6 | 7,0 | 0,6 | 15 | 13 | 2 |
| | 2,78 | 3,2 | 2,2 | 1,5 | 0,7 | 1,1 | 74283 | 16287 | 90569 | 7,1 | 6,5 | 0,7 | 15 | 13 | 2 |
| | 3,58 | 3,2 | 2,2 | 1,6 | 0,7 | 1,0 | 72672 | 16543 | 89215 | 7,4 | 7,4 | 0,0 | 16 | 12 | 3 |
| | 4,08 | 3,4 | 2,0 | 1,4 | 0,6 | 1,4 | 70738 | 19376 | 90115 | 7,9 | 6,9 | 1,0 | 16 | 12 | 4 |
| | 5,05 | 3,2 | 2,6 | 1,9 | 0,7 | 0,6 | 80237 | 11978 | 92215 | 8,1 | 6,9 | 1,2 | 16 | 13 | 3 |
| | 5,98 | 3,2 | 2,6 | 1,9 | 0,7 | 0,6 | 79977 | 11509 | 91486 | 7,4 | 8,1 | 0,0 | 16 | 13 | 3 |
| | 21,22 | 3,2 | 2,0 | 1,4 | 0,6 | 1,2 | 68164 | 23959 | 92123 | 8,1 | 7,1 | 1,1 | 15 | 12 | 3 |
| | 24,23 | 3,2 | 2,4 | 1,5 | 0,8 | 0,9 | 70836 | 19412 | 90248 | 7,2 | 6,8 | 0,4 | 15 | 12 | 3 |
| | 44,33 | 3,3 | 2,3 | 1,6 | 0,7 | 1,0 | 69264 | 21563 | 90827 | 7,1 | 6,5 | 0,6 | 18 | 14 | 5 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 45,48 | 3,4 | | | | | | | | 7,4 | | | 18 | | |
| | Lake | 0,6 | 0,5 | 0,4 | 0,1 | 0,0 | 0 | 0 | 0 | 0,6 | 0,7 | 0,0 | 4 | 3 | 1 |
| **Desorption part** | 0,1 | 0,6 | 0,6 | 0,4 | 0,3 | 0,0 | 376 | 392 | 768 | 0,8 | 0,8 | 0,0 | 4 | 2 | 2 |
| | 0,2 | 0,6 | 0,6 | 0,3 | 0,4 | 0,0 | 362 | 339 | 700 | 0,7 | 0,7 | 0,1 | 4 | 2 | 2 |
| | 0,4 | | 0,7 | 0,4 | 0,3 | | 427 | 326 | 753 | 0,7 | 0,6 | 0,1 | 3 | 2 | 1 |
| | 1,2 | | 0,5 | 0,4 | 0,1 | | 536 | 346 | 882 | 0,7 | 0,6 | 0,2 | | | |
| | 2,2 | | 0,7 | 0,4 | 0,2 | | 642 | 345 | 987 | | | | | | |
| | 3,1 | | 0,5 | 0,5 | 0,1 | | 725 | 380 | 1105 | 0,9 | 0,7 | 0,1 | | | |
| | 4,1 | | 0,6 | 0,4 | 0,1 | | 831 | 374 | 1206 | 0,7 | 0,6 | 0,1 | | | |
| | 19,0 | | 0,6 | 0,5 | 0,1 | | 1597 | 584 | 2181 | 0,8 | 0,8 | 0,0 | | | |
| | 21,9 | | 0,5 | 0,4 | 0,1 | | 1767 | 644 | 2411 | 0,8 | 0,7 | 0,1 | | | |
| | 43,2 | | 0,6 | 0,5 | 0,1 | | 2083 | 731 | 2814 | 0,8 | 0,9 | 0,0 | | | |
| | 47,8 | 0,7 | 0,6 | 0,5 | 0,1 | 0,1 | 2107 | 738 | 2844 | 1,0 | 0,9 | 0,1 | | | |
| | 123,8 | 0,8 | 0,7 | 0,5 | 0,1 | 0,1 | 2347 | 1204 | 3551 | 0,7 | 0,8 | 0,0 | | | |
| | 124,1 | 0,8 | 0,6 | 0,6 | 0,1 | 0,1 | 2416 | 1227 | 3643 | 0,7 | 0,7 | 0,0 | 4 | 2 | 2 |
| | 164,2 | 0,8 | 0,7 | | | 0,2 | 2445 | 1230 | 3675 | 0,8 | 0,8 | 0,0 | 4 | 2 | 2 |
| | 164,5 | 0,7 | 0,6 | | | 0,1 | 2428 | 1206 | 3634 | 0,9 | 0,8 | 0,0 | 4 | 2 | 2 |
| | 381,5 | | | 0,5 | | | 2540 | 1356 | 3896 | 0,8 | 0,7 | 0,1 | | | |
| | 381,6 | | | 0,5 | | | 2561 | 1348 | 3909 | 0,7 | 0,7 | 0,0 | | | |

*Table 8-20: Raw data for fractionation of pH, conductivity and absorbance in the Low P concentration II water-mixing experiment.*

| | Time hours | conductivity µS/cm | pH | TNOM Abs254 | TNOM Abs400 | TNOM Abs600 | TNOM SAR | DNOM Abs254 | DNOM Abs400 | DNOM Abs600 | DNOM SAR | PNOM △Abs254 | PNOM △Abs400 | PNOM SAR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Starting conditions** | Agriculture | 153 | 6,9 | 0,520 | 0,084 | 0,013 | 6,2 | 0,342 | 0,034 | 0,003 | 10,2 | 0,179 | 0,051 | 3,5 |
| | Forest | 59 | 5,5 | 0,628 | 0,073 | 0,007 | 8,6 | 0,610 | 0,070 | 0,007 | 8,8 | 0,019 | 0,003 | 5,3 |
| | Agriculture added 32P | 155 | 7,1 | 0,517 | 0,085 | 0,013 | 6,1 | 0,374 | 0,042 | 0,004 | 9,0 | 0,144 | 0,044 | 3,3 |
| | Forest added Al | 63 | 4,8 | 0,622 | 0,074 | 0,007 | 8,4 | 0,611 | 0,070 | 0,006 | 8,8 | 0,012 | 0,004 | 2,6 |
| | Conservative mix | 109 | 5,1 | 0,570 | 0,080 | 0,010 | 7,2 | 0,492 | 0,056 | 0,005 | 8,9 | 0,078 | 0,024 | 3,2 |
| **Mixing Part** | 0,03 | 107 | 6,4 | 0,581 | 0,083 | 0,011 | 7,0 | 0,515 | 0,062 | 0,006 | 8,4 | 0,067 | 0,022 | 3,1 |
| | 0,15 | 107 | 6,5 | 0,585 | 0,083 | 0,011 | 7,0 | 0,502 | 0,059 | 0,005 | 8,6 | 0,084 | 0,025 | 3,4 |
| | 0,27 | 107 | 6,6 | 0,585 | 0,084 | 0,011 | 7,0 | 0,514 | 0,061 | 0,005 | 8,5 | 0,072 | 0,024 | 3,0 |
| | 0,38 | 107 | 6,7 | 0,585 | 0,085 | 0,012 | 6,9 | 0,512 | 0,061 | 0,005 | 8,5 | 0,074 | 0,025 | 3,0 |
| | 0,65 | 107 | 6,8 | 0,586 | 0,085 | 0,012 | 6,9 | 0,508 | 0,061 | 0,005 | 8,4 | 0,079 | 0,025 | 3,2 |
| | 0,85 | 108 | 6,8 | 0,587 | 0,085 | 0,011 | 6,9 | 0,509 | 0,061 | 0,005 | 8,4 | 0,079 | 0,025 | 3,2 |
| | 1,00 | 108 | 6,9 | 0,586 | 0,085 | 0,011 | 6,9 | 0,509 | 0,061 | 0,005 | 8,4 | 0,078 | 0,025 | 3,2 |
| | 1,60 | 108 | 6,6 | 0,591 | 0,085 | 0,011 | 7,0 | 0,513 | 0,062 | 0,005 | 8,3 | 0,079 | 0,024 | 3,3 |
| | 2,07 | 108 | 6,9 | 0,582 | 0,086 | 0,0 | 6,8 | 0,501 | 0,061 | 0,005 | 8,3 | 0,082 | 0,026 | 3,2 |
| | 2,78 | 110 | 7,0 | 0,59 | 0,087 | 0,012 | 6,8 | 0,516 | 0,062 | 0,005 | 8,4 | 0,075 | 0,026 | 2,9 |
| | 3,58 | 110 | 7,0 | 0,59 | 0,087 | 0,013 | 6,8 | 0,506 | 0,061 | 0,005 | 8,4 | 0,085 | 0,027 | 3,2 |
| | 4,08 | 111 | 7,3 | 0,585 | 0,087 | 0,011 | 6,7 | 0,499 | 0,059 | 0,005 | 8,5 | 0,087 | 0,029 | 3,0 |
| | 5,05 | 116 | - | 0,59 | 0,088 | 0,012 | 6,7 | 0,535 | 0,068 | 0,006 | 7,9 | 0,056 | 0,021 | 2,7 |
| | 5,98 | 119 | 6,9 | 0,588 | 0,087 | 0,011 | 6,8 | 0,536 | 0,068 | 0,006 | 7,9 | 0,053 | 0,020 | 2,7 |
| | 21,22 | 113 | 6,9 | 0,589 | 0,089 | 0,012 | 6,6 | 0,512 | 0,061 | 0,005 | 8,4 | 0,077 | 0,028 | 2,8 |
| | 24,23 | 115 | - | 0,592 | 0,091 | 0,012 | 6,5 | 0,513 | 0,063 | 0,005 | 8,1 | 0,079 | 0,028 | 2,8 |
| | 44,33 | 102 | 7,3 | 0,595 | 0,09 | 0,014 | 6,6 | 0,531 | 0,066 | 0,005 | 8,0 | 0,064 | 0,024 | 2,7 |
| | 45,48 | 101 | 7,1 | 0,595 | 0,092 | 0,015 | 6,5 | | | | | | | |
| | Lake | 93 | 6,9 | 0,325 | 0,037 | 0,007 | 8,8 | 0,299 | 0,027 | 0,002 | 11,1 | 0,026 | 0,010 | 2,6 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Desorption part** | 0,1 | 93 | 6,9 | 0,325 | 0,036 | 0,006 | 9,0 | 0,314 | 0,029 | 0,002 | 10,8 | 0,011 | 0,007 | 1,6 |
| | 0,2 | 92 | 6,9 | 0,327 | 0,035 | 0,006 | 9,3 | 0,312 | 0,029 | 0,001 | 10,8 | 0,015 | 0,006 | 2,5 |
| | 0,4 | 92 | 7,0 | 0,324 | 0,037 | 0,006 | 8,8 | 0,313 | 0,029 | 0,001 | 10,8 | 0,011 | 0,008 | 1,4 |
| | 1,2 | 108 | 7,1 | 0,325 | 0,036 | 0,006 | 9,0 | 0,313 | 0,029 | 0,001 | 10,8 | 0,012 | 0,007 | 1,7 |
| | 2,2 | 109 | 7,1 | 0,324 | 0,037 | 0,006 | 8,8 | 0,313 | 0,029 | 0,001 | 10,8 | 0,011 | 0,008 | 1,4 |
| | 3,1 | 111 | 7,0 | 0,324 | 0,037 | 0,006 | 8,8 | 0,312 | 0,029 | 0,002 | 10,8 | 0,012 | 0,008 | 1,5 |
| | 4,1 | 111 | 7,0 | 0,327 | 0,038 | 0,007 | 8,6 | 0,313 | 0,029 | 0,002 | 10,8 | 0,014 | 0,009 | 1,6 |
| | 19,0 | 114 | 6,7 | 0,333 | 0,038 | 0,007 | 8,8 | 0,318 | 0,029 | 0,002 | 11,0 | 0,015 | 0,009 | 1,7 |
| | 21,9 | 112 | 7,0 | 0,333 | 0,039 | 0,007 | 8,5 | 0,315 | 0,029 | 0,002 | 10,9 | 0,018 | 0,010 | 1,8 |
| | 43,2 | 108 | 7,1 | 0,334 | 0,039 | 0,006 | 8,6 | 0,322 | 0,030 | 0,003 | 10,7 | 0,012 | 0,009 | 1,3 |
| | 47,8 | 114 | 7,1 | 0,336 | 0,04 | 0,007 | 8,4 | 0,320 | 0,030 | 0,003 | 10,7 | 0,016 | 0,010 | 1,6 |
| | 123,8 | 109 | 6,8 | 0,342 | 0,042 | 0,007 | 8,1 | 0,322 | 0,030 | 0,002 | 10,7 | 0,020 | 0,012 | 1,7 |
| | 124,1 | 108 | 7,0 | 0,345 | 0,042 | 0,007 | 8,2 | 0,327 | 0,030 | 0,002 | 10,9 | 0,018 | 0,012 | 1,5 |
| | 164,2 | 115 | 7,2 | | | | | | | | | | | |
| | 164,5 | 116 | 7,2 | | | | | | | | | | | |
| | 381,5 | 118 | 7,1 | 0,336 | 0,041 | 0,007 | 8,2 | 0,323 | 0,031 | 0,003 | 10,4 | 0,013 | 0,010 | 1,3 |
| | 381,6 | 119 | 7,2 | 0,338 | 0,043 | 0,008 | 7,9 | 0,316 | 0,030 | 0,002 | 10,5 | 0,022 | 0,013 | 1,7 |

*Table 8-21: Raw data for fractionation of phosphorus, radioactive phosphorus and aluminium in the High P concentration II water-mixing experiment.*

| | | Phosphorus | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Experiment time** | **TP µmol/L** | **TDP µmol/L** | **DRP µmol/L** | **DOP µmol/L** | **PP µmol/L** | **Alaf µmol/L** | **Alof µmol/L** | **Alif µmol/L** | **Alr µmol/L** | **Alrf µmol/L** | **Particulate Al µmol/L** |
| **Starting conditions** | Agriculture | 6,5 | 4,9 | 3,8 | 1,1 | 1,6 | 1,6 | 0,6 | 1,0 | 5 | 4 | 1 |
| | Forest | 0,4 | 0,2 | 0,2 | 0,0 | 0,2 | 12,3 | 7,7 | 4,6 | 13 | 14 | 0 |
| | Agriculture added P | 11,3 | 9,6 | 8,7 | 0,9 | 1,7 | 1,3 | 0,4 | 0,9 | | | |
| | Forest added Al | 0,3 | 0,2 | 0,2 | 0,0 | 0,1 | 39,6 | 15,1 | 24,5 | 38 | 40 | 0 |
| | Conservative mix | 5,8 | 4,9 | 4,5 | 0,4 | 0,9 | 20,4 | 7,8 | 12,7 | 21 | 22 | 0 |
| **Mixing part** | 0,05 | 7,3 | 4,7 | 3,9 | 0,8 | 2,6 | 16,0 | 11,8 | 4,2 | | | |
| | 0,05 | 6,1 | 5,0 | 4,1 | 0,9 | 1,1 | | | | | | |
| | 1,4 | 5,8 | 4,6 | 3,9 | 0,7 | 1,1 | 16,0 | 12,3 | 3,7 | | | |
| | 1,4 | 5,8 | 4,7 | 4,1 | 0,6 | 1,1 | 14,9 | | | | | |
| | 21,6 | 5,8 | 4,5 | 3,8 | 0,7 | 1,3 | 13,4 | 10,5 | 2,9 | | | |
| | 21,6 | | | | | | 11,9 | 10,0 | 1,9 | | | |

*Table 8-22: Raw data for fractionation of pH, conductivity and UV-Vis absorbance in the High P concentration water-mixing experiment.*

| | | | | TNOM | | | | DNOM | | | | PNOM | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Experiment time** | **conductivity µS/cm** | **pH** | **Abs254** | **Abs400** | **Abs600** | **SAR** | **Abs254** | **Abs400** | **Abs600** | **SAR** | **ΔAbs254** | **ΔAbs400** | **SAR** |
| Starting conditions | Agriculture | 141 | 6,8 | 0,541 | 0,098 | 0,005 | 5,5 | 0,482 | 0,074 | 0,005 | 6,5 | 0,059 | 0,024 | 2,5 |
| | Forest | 53 | 5,7 | 0,644 | 0,08 | 0,005 | 8,1 | 0,635 | 0,078 | 0,005 | 8,1 | 0,009 | 0,002 | 4,5 |
| | Agriculture added P | 148 | 6,8 | 0,522 | 0,089 | 0,016 | 5,9 | 0,481 | 0,064 | 0,007 | 7,5 | 0,041 | 0,025 | 1,6 |
| | Forest added Al | 127 | 3,8 | 0,596 | 0,07 | 0,007 | 8,5 | 0,589 | 0,065 | 0,006 | 9,1 | 0,007 | 0,005 | 1,4 |
| | Conservative mix | 137 | 4,1 | 0,559 | 0,080 | 0,012 | 7,2 | 0,535 | 0,065 | 0,007 | 8,3 | 0,024 | 0,015 | 1,6 |
| Mixing part | 0,05 | 113 | 5,6 | 0,571 | 0,085 | 0,012 | 6,7 | 0,533 | 0,066 | 0,006 | 8,1 | 0,038 | 0,019 | 2,0 |
| | 0,05 | 116 | 6,0 | 0,572 | 0,083 | 0,012 | 6,9 | 0,525 | 0,066 | 0,006 | 8,0 | 0,047 | 0,017 | 2,8 |
| | 1,4 | 116 | 6,0 | 0,572 | 0,083 | 0,012 | 6,9 | 0,611 | 0,065 | 0,006 | 9,4 | | 0,018 | |
| | 1,4 | 108 | 6,1 | 0,575 | 0,084 | 0,012 | 6,8 | 0,544 | 0,069 | 0,007 | 7,9 | 0,031 | 0,015 | 2,1 |
| | 21,6 | 88 | 6,1 | | | | | | | | 0,0 | | | |
| | 21,6 | | | 0,583 | 0,086 | 0,011 | 6,8 | 0,545 | 0,068 | 0,005 | 8,0 | 0,038 | 0,018 | 2,1 |

## 8.5 Quality control

### 8.5.1 Blanks and standards

Method blanks were measured for about every $10^{th}$ sample taken. For spectrometric measurements standard curve was measured at the beginning and the end of the day, and also some single standards during the day to assure that absorbance was constant. For determination of limit of detection and limit of quantification, three times and ten times the standard deviation of ten blanks were used, respectively. Experiment samples that in time were taken long after other samples were taken in duplicates to eliminate/detect random errors.

For characterization of samples, filtered and not filtered deionized water were included as blanks to control contamination from filtration and instrument blank value.

Standard curves were made so that samples always were inside the concentration range of the lowest (excluding the 0 standard) and the highest standard.

All atomic weights used in calculations are taken from periodesystemet.no.

### 8.5.2 Check of outliers

For analytical measurements with more than three replicates, a Grubbs test with $p < 0.05$ was performed to check for outliers (Miller & Miller, 2005). This test assumes that the values are normally distributed. Outliers are only rejected in samples sizes above 3, as the rejection of one value on the basis of only two other can give a less reliable mean estimate (Miller & Miller, 2005).

### 8.5.3 Testing that slope is significantly different from 0

To see if there is any change with time in the sorption-desorption experiments, a test is conducted to see if the slope from the linear regression on logarithmic time scale is significantly different from zero.

$$t = \frac{\beta}{se(\beta)}$$

β is the slope and se(β) is the standard error for the slope. When t is high, the null hypothesis – that the slope is zero – is rejected.

### 8.5.4 Counting of radioactivity

Counting of radioactivity is poisson distributed. To reduce the uncertainty in the measurements, each sample was counted until 50 000 counts.

To ensure that what is counted is not only background signals, vials without radioactivity were counted to detect the background activity, which was generally found to be below 200 DPM. More importantly, energy spectra of the counted disintegrations were inspected to see that the signal was not only background noise.

Vials were wiped with Kleenex to avoid scattering of light due to fingerprints and dust. To reduce chemiluminescence and bubbles samples were left inside instrument for one hour before measurement.

## 8.6 Quench correction

Challenges in LSC include background from unwanted radioactivity, chemiluminescence, bioluminescence, quenching of light and electrical noise and related problems. Quenching is any phenomena which absorbs or hinders light from the scintillation process to reach the light detecting photo-multiplier tubes (PMTs). Thus, quenching will result in a weaker signal from the PMTs making the distribution of counts in the energy spectrum shifts towards lower energy (see Figure 8-10).

Because there is a lower limit of light (number of photons) that will be detectable due to the detector response function and electronic noise, quenching can reduce the amount of light from low-energy events so much that these events no longer are detected by the PMTs. This reduces the number of counts observed by the LSC system, making it seem like there is less activity present in the sample than it really is. Quenching can inter alia be caused by colloidal particles or by a coloured sample, with yellow as a specific problematic colour as this absorbs photon in the same energy region as the scintillation molecules emits. In both cases light is

absorbed between the emitting scintillator molecule and the PMT. Quenching can also be "chemical", which means that one or more parts of the scintillator cocktail is chemically changed in such a way that the light emission is reduced. There is humus in the water samples used for these experiments, which colours the samples yellow. Measurements were also performed on filter papers, and these can interfere with the light. Thus, some quenching was expected.

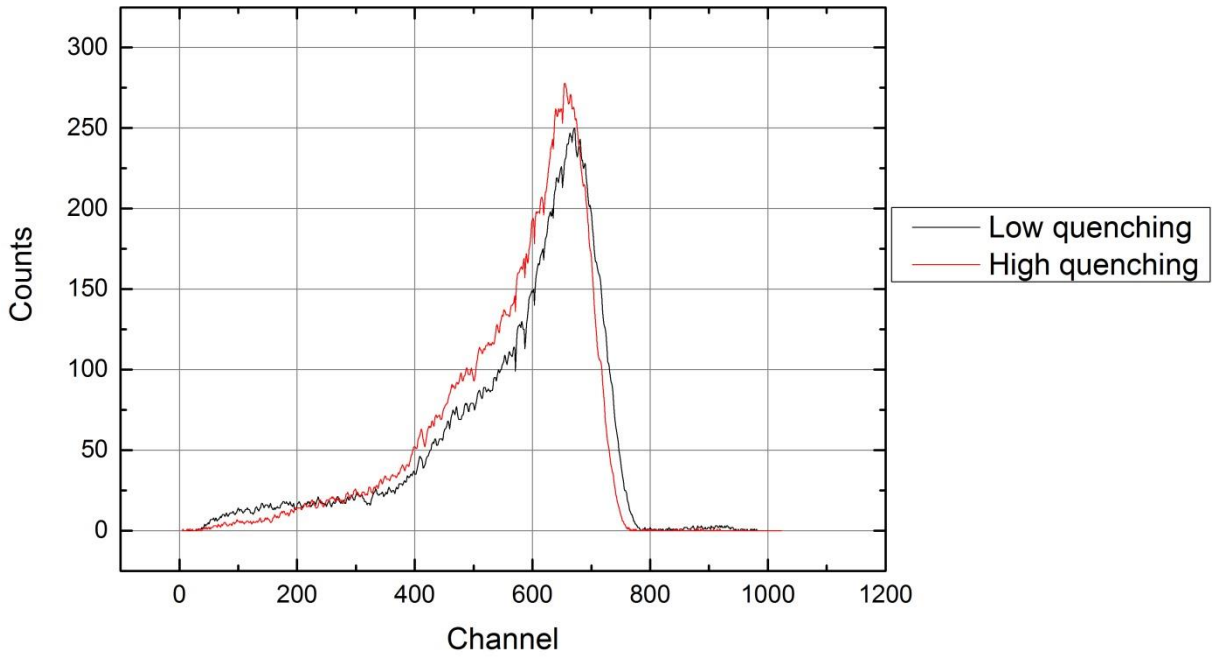


*Figure 8-10: The least and most quenched samples in the quenching test.*

Two different methods was used to investigate the quenching of the samples; the Channel Ratio method and Triple to Double Coincidence Ratio (TDCR). Quench correction is done in order to know the true activity in a quenched sample.

Both the channel ratio method and the TDCR method were shown to be reliable (see the next two paragraphs), and as the TDCR method is a standard part of the measurements by the LSC instrument, this method is used.

### 8.6.1 Triple to Double Coincidence Ratio (TDCR)

To rule out noise, liquid scintillation counters normally have two detectors. If only one of the detectors register light, it is probably stray light, and the event is not counted as the disintegration of an atom. The Liquid scintillation counter used in this experiment has three photo multiplier tubes (PM-tubes). Light should spread in all directions and be detected by all

three detectors, but if there is quenching in the sample the detector that is furthest away might not register the disintegration event as not enough light reaches it. The ratio between the counts detected by all three detectors and the counts detected by two – the *Triple to Double Coincidence Ratio* (TDCR) – can thus be used as a measure of the quenching in the sample (Southern Scientific Ltd, 2012). For pure β-emitting radionuclides the TDCR is directly proportional to the efficiency (Southern Scientific Ltd, 2012). The efficiency is the fraction of disintegrations that are counted; it is equal to one when all disintegrations are registered.

Figure 8-11 shows all the TDCR values measured during the three water-mixing experiments where radioactivity was used. Results are separated into filtrate and filter papers. In the beginning of the desorption part of the experiment, the activity in the water samples is very low (300-800 counts per minute, CPM), and these are the measurements seen on the left with lower TDCR values. All measurements with activity above 1500 CPM have TDCR values > 0.98. This supports that there is low quenching in the samples, and the low variation in TDCR values suggests that this is a reproducible method for measuring quenching; the samples are quenched equally in the same matrix.

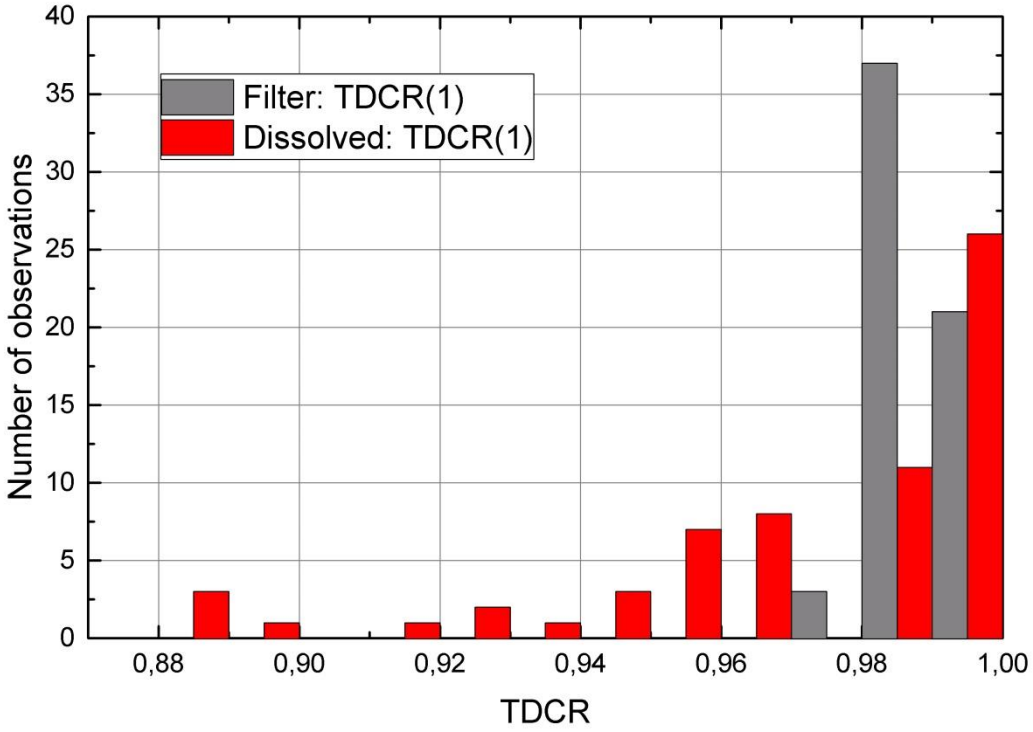

*Figure 8-11: Histogram of TDCR values for all the LSC measurements from the water-mixing experiment. The distribution is wider for the water sample than for the filter paper samples.*

Investigations were performed to validate the TDCR method. $CCl_4$ was added in different amounts to samples with constant activity, and the activity was measured. The TDCR values were compared with the efficiency of the measurement, giving a close to linear plot, with a visible curvature only with highly quenched samples, see Figure 8-12. This means that the TDCR method for quench correction safely can be used for the samples in this experiment, which all have a TDCR value above 0.88.

TDCR was also measured together with the quench correction curve described in Paragraph 8.6.2 (see Table 8-23) but the quenching was lower than the 5 % uncertainty of the method (TDCR > 0.97), and thus the results were not useful.

The TDCR method is reported to be accurate to 5 % (Southern Scientific Ltd, 2012), which is considered satisfying for the purpose of these investigations. Thus, the quench corrected activity (disintegrations per minute, DPM) calculated by the instrument based on the TDCR value is used in the results.

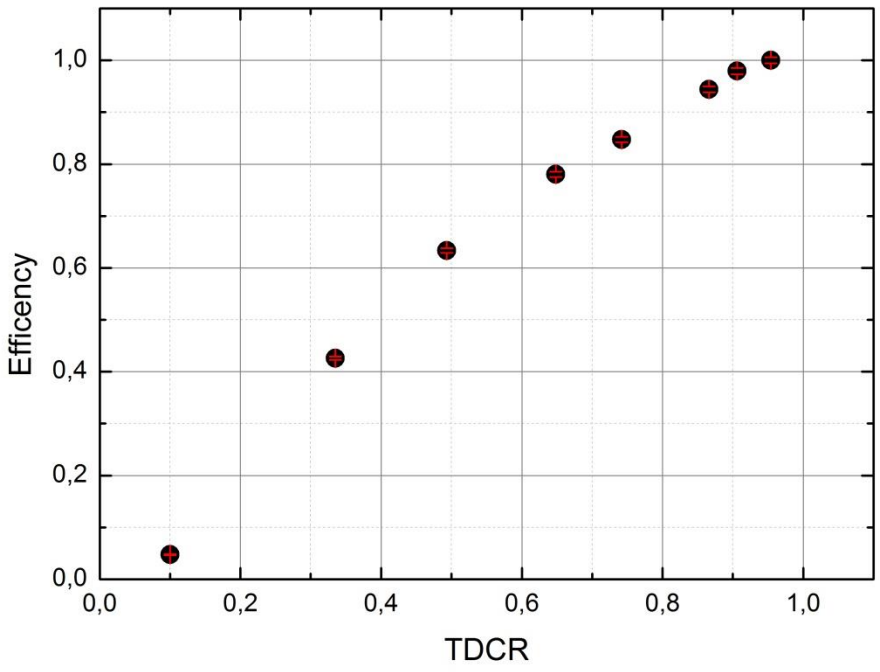


*Figure 8-12: Efficiency versus triple to double coincidence ratio (TDCR) measured for samples quenched with $CCl_4$.*

### 8.6.2 Sample-Channels Ratio Method

The *Sample-Channels Ratio Method* utilizes the fact that the distribution of counts from a β emitter is displaced toward lower energy channels when quenching occurs (see Figure 8-10). The proportion of counts in the lower part of the energy spectrum increases as the quenching increases (see Figure 8-10). This can be utilized to make a quench curve showing the relationship between the energy distribution of the counts and the quenching, and knowing this relationship makes us able to determine the true activity in samples with unknown quenching. The quench curve is made by measuring a series of samples with different degrees of quenching. The samples should only differ in the degree of quenching. The energy distribution expressed by the channel ratio, which is obtained by dividing the spectrum in two parts and calculate the ratio between them. The curve is made by plotting counting efficiency as a function of channel ratio.

To make a quench correction curve, 10 vials were added different volumes of water from a water-mixing experiment containing $^{32}P$ and deionized water to a total volume of 10 mL. 10 mL of Gold Star Multipurpose LS Cocktail from Meridian was added to each vial. In order to check the repeatability, three replicates were made of the biggest and the smallest volume.

Results from the counting are shown in Table 8-23.

*Table 8-23: Results from counting of samples for quench correction curve. The first column states how many mL of experiment sample that was added. Higher sample volume gives higher quenching. To achieve a constant volume, deionized water was added to get a total of 10 mL.*

| Added sample (mL) | Channel 5-600 (counts) | Channel 601-950 (counts) | TDCR |
|---|---|---|---|
| 1 | 22834 | 27420 | 0,970 |
| 1 | 22904 | 27421 | 0,970 |
| 1 | 22958 | 27257 | 0,970 |
| 3 | 23421 | 27662 | 0,986 |
| 5 | 24376 | 27443 | 0,987 |
| 7 | 24736 | 26424 | 0,990 |
| 9 | 26541 | 26828 | 0,989 |
| 10 | 27034 | 27190 | 0,990 |
| 10 | 27356 | 26810 | 0,991 |
| 10 | 27345 | 26518 | 0,989 |

The three replicates for 1 and 10 mL of added sample had relative standard deviations for CPM of 0.9 % and 0.4 % respectively. Thus, the repeatability is good.

The channel ratio is plotted against the efficiency to make a quench correction curve. The true activity in this case is unknown, and is estimated by the average of the CPM from three least quenched samples (1 mL sample and 9 mL deionized water), and the efficiency of a sample is its CPM divided by this value. The channel ratio is the ratio of the chosen channel regions:

$$Channel\ ratio = \frac{Number\ of\ counts\ in\ channels\ 5-600}{Number\ of\ counts\ in\ channels\ 601-950}$$

Thus, higher channel ratio means there are more counts in the low energy region, indicating higher quenching. Figure 8-13 shows the efficiency as a function of the channel ratio. As expected, the efficiency decreases as the channel ratio increases.

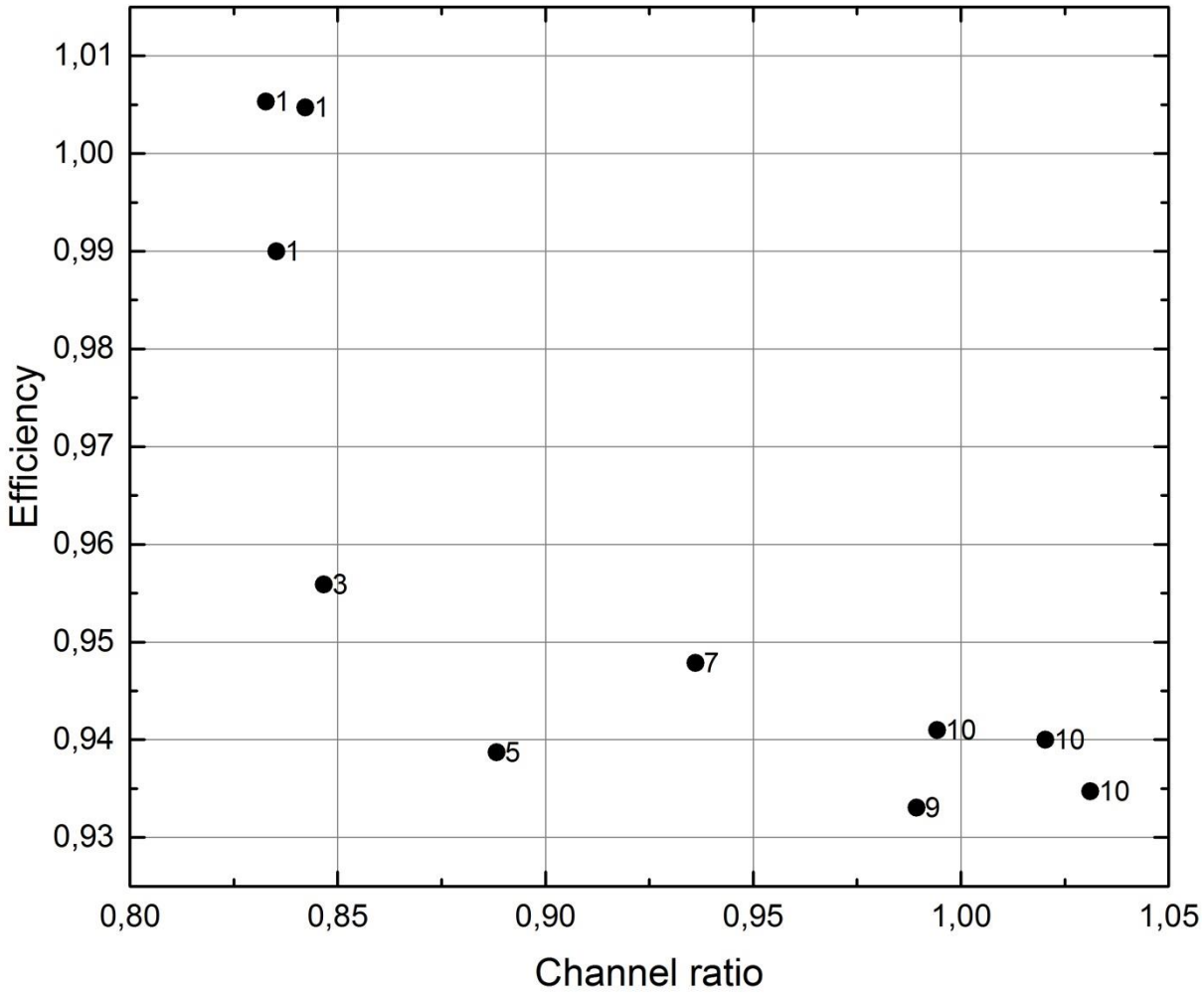

*Figure 8-13: Efficiency as a function of channel ratio for the samples prepared to investigate the quenching. The labels of the points show the volume (mL) of sample that was added, indicating the expected degree of quenching.*

## 8.7 Selection of filter paper for experiments

There were several challenges regarding the type of filter material to use in this study (see Table 8-24). The common operational definition for particles is what does not pass through a 0.45 µm filter paper. Glass fibre filter paper is preferred for the liquid scintillation counting (LSC) as it does not interfere with the emitted light as a membrane filter paper will do. On the other hand glass fibre filter paper is not available with 0.45 µm pore size. Cellulose nitrate (CN) membranes are generally not recommended for filtering solutions where protein binding is a concern. This may represent a problem for these samples containing DOM. Instead Cellulose acetate (CA) membranes have a very low binding affinity for most macromolecules and are especially recommended for applications requiring low protein binding[2]. Table 4-1 shows an overview of the filters that have been used, and the challenges that were encountered. For the sorption-desorption experiments (blank, low concentration and high concentration) a 0.45 µm Cellulose Nitrate Filter from Sartorius (Cat. no. 13906 47 ACN) was used, but when a new pack of filter paper was used, the absorbance for the DTP blanks increased 10 times. These filter papers are not tested for what they desorb during filtration, and are thus not intended for use were the filtrate is to be analysed – like in the experiments performed in this thesis. Thus, more suitable filter papers had to be found.

As can be seen from Chapter 5.1.1, no significant differences was found between weight of the retained particles between the GF, M and S filters.

Total suspended solids (TSS) were measured with three different filter papers to see if there was any difference in what the filters retained: 0.7 µm GF/F Glass Microfibre filter from Whatman (Cat. No 1825-047), 0.45 µm HAWP MF-Millipore Membrane (Cat. No. HAWP04700 and 0.45 µm Supor® polyethersulfone membrane filters from Pall. No significant differences were found.

A sorption-desorption experiment was conducted to test if filters with different pore-size (0.45 and 0.7 µm) would give comparable results. A 0.45 µm Cellulose Acetate membrane filter

[2] http://www.cultek.com/pdf/t_filterselectionguide.pdf

from Sartorius (Cat. no. 11106 47 ACN) and a 0.7 µm GF/F Glass Microfibre filter from Whatman (Cat. No 1825-047) were compared. The GF filter did indeed lead to apparently higher DRP and DTP concentrations (5.3.3.4). These results were confirmed by tests with radioactive phosphorus (though with 0.45 µm Supor® polyethersulfone membrane filters from Pall), see Appendix, Paragraph 8.8.

*Table 8-24: Table 4-1, repeated for readability. Overview of the filter papers that have been used, what they were used for, and problems that were encountered.*

| Filter paper | Pore size (µm) | Experiment | Problem |
|---|---|---|---|
| Cellulose Nitrate (CN) | 0.45 | Sorption Characterization | Contamination |
| Cellulose Acetate (CA) | 0.45 | Sorption (filter comparison) | |
| Glass Fibre (GF) | 0.7 | Sorption (filter comparison), Water-mixing Comparison with S filters | Pore size |
| MF Millipore (M) | 0.45 | Water mixing, Characterization | |
| Supor® Polyethersulfone (S) | 0.45 | Characterization Comparison with GF filters | Slow filtration |

*CN: Cellulose Nitrate 0.45 µm filter from Sartorius (Cat. no. 13906 47 ACN)*
*AC: Cellulose Acetate 0.45 µm filter from Sartorius (Cat. no. 11106 47 ACN)*
*GF: GF/F Glass Microfibre 0.7 µm filters from Whatman (Cat. No 1825-047)*
*S: Supor®-450 Polyethersulfone 0.45 µm membrane filter from Pall (P/N 60173)*
*M: HAWP MF-Millipore 0.45 µm membrane filter (Cat. No. HAWP04700)*

The water-mixing experiment including radioactivity was started (blank and high P concentration experiment) using 0.7µm GF/F Glass Microfibre Filters from Whatman (Cat. No 1825-047) in order to avoid interference during the liquid scintillation counting (LSC). The expected decrease in P concentration was not seen in the water-mixing experiments performed with GF filter papers, and this raised the possibilities that the particles between 0.7 and 0.45 µm could be important for the experiment. The 0.45µm membrane filters Supor® polyethersulfone (S) were recommended by VWR for the experiments. As membrane filter paper can cause interference with the LSC measurements, tests to show reproducible counting results were performed (see Paragraph 8.8). The next part of the water-mixing experiment (low P concentration I) was thus started with the S filter papers. It soon proved impossible to use as the filtration time was too long (> 30 min for the 200 mL necessary for the experiment).

Yet another 0.45µm filter paper (HAWP MF-Millipore Membrane (Cat. No. HAWP04700) was used from the second replicate of this experiment. The Millipore filter paper gave rapid filtering and reproducible results for counting on the LSC (see Paragraph 8.8).

### 8.7.1 Test of 0.7 versus 0.45 µm filter papers

The difference between 0.45 µm and 0.7 µm filter papers have been investigated twice in this work: in the filter paper comparison sorption-desorption experiment (see Chapter 5.3.3.4) and with leftover water from one of the water-mixing experiments, see below.

Appendix, Paragraph 8.8 shows that the 0.7 µm GF/F Whatman filter papers let through almost twice as much radiation as the 0.45 µm µm Supor® membrane filter papers (see Table 8-25, Table 8-26 and Table 8-27). In total 44 % of the activity was considered dissolved in the tests with the 0.7 µm filter, while the corresponding values for the 0.45µm filter was 27 and 29 %. This was thought to be part of the reason for unexpected results in the mixing experiment, but replacing the 0.7µm filter with 0.45 µm pore size filter did not change the results. Instead, a higher than optimal pH is thought to have at least partly caused the unexpected results.

Also the filter comparison experiment gave significantly different results for the two different pore sizes. It is therefore concluded that the use of filter paper with 0.45 µm or 0.7 µm pore size will give significantly different results.

## 8.8 Test of filter papers for LSC

### 8.8.1 Purpose

Glass fibre filter papers are normally preferred in LSC as these filter papers interfere less with the light that is produced, but these filter papers are not available with 0.45 µm pore size. Particulate material is here defined as what does not pass through a 0.45 µm filter paper, thus this pore size is the preferred, and we wanted to see if it was possible to reproducibly count membrane filter papers with liquid scintillation counting (LSC).

For comparison, some measurements were also made with glass fibre filter paper.

### 8.8.2 Method

#### 8.8.2.1 Supor® and GF filter papers

Leftover water from the mixing part of the Blank water-mixing experiment was filtered with Supor® and GF filter papers about one month after the experiment was ended.

100 mL of water was filtered through a 0.45 µm Supor® polyetersulfon filter from Pall. 10 mL of the water was taken for counting with liquid scintillation counting (LSC) after mixing with 10 mL of Gold Star Multi Purpose LS cocktail from Meridian. The filter paper was either added 10 mL water and 10 mL of Gold Star Multi Purpose LS cocktail from Meridian or only 10 mL Filter Count from Perkin Elmer. 5 replicates were made of each.

The process was repeated with Whatman GF/F filter papers. Three replicates were made, and all were counted with Gold Star Multi Purpose LS cocktail from Meridian.

#### 8.8.2.2 Millipore filter papers

Leftover water from the desorption part of the Low P concentration I water-mixing experiment was filtered with 0.45 µm HAWP MF-Millipore Membrane filter papers (Cat. No. HAWP04700). 100 mL of water was filtrated through a 0.45 µm Millipore filter, and the filter was taken for counting. The water phase was not counted. The filter paper was either added 10 mL water and 10 mL of Gold Star Multi Purpose LS cocktail from Meridian or only 10 mL Filter Count from Perkin Elmer. 3 replicates were made of each.

### 8.8.3 Results

Table 8-25 shows the results for samples filtered with Supor® filter paper, and Gold star multipurpose scintillation liquid used for counting of both water and filter papers.

*Table 8-25: Results for filtration with Supor® filter paper and Gold star multipurpose scintillation liquid used for counting for both water and filter papers.*

| Replicate | Water activity (CPM) | Filter activity (CPM) | Particulate : dissolved |
|---|---|---|---|
| 1 | 4468 | 11901 | 2,66 |
| 2 | 4794 | 11707 | 2,44 |
| 3 | 4936 | 11798 | 2,39 |
| 4 | 5897 | 12664 | 2,15 |
| 5 | 4736 | 12734 | 2,69 |
| Average (CPM) | 4966 | 12161 | 2,47 |
| Stdev (CPM) | 547 | 497 | 0,2 |
| Rstdev (%) | 11 % | 4,1 % | 9 % |

Table 8-26 shows the results for samples filtrated with Supor® filter paper, and Gold star multipurpose Scintillation liquid for water and Filter Count scintillation liquid for filter papers.

*Table 8-26: Results for filtration with Supor® filter paper and Gold star multipurpose scintillation liquid for water and Filter Count scintillation liquid for filter papers.*

| Replicate | Water activity | Filter activity | Fraction particulate |
|---|---|---|---|
| 1 | 4736 | 13329,1 | 2,81 |
| 2 | 4846 | 12599,4 | 2,60 |
| 3 | 4736 | 14277,8 | 3,01 |
| 4 | 4864 | 12730,1 | 2,62 |
| 5 | 4841 | 13224,7 | 2,73 |
| Average | 4805 | 13232 | 2,76 |
| Stdev | 63 | 662 | 0,2 |
| Rstdev | 1 % | 5,0 % | 6 % |

Table 8-27 shows the results for samples filtrated with Whatman GF/F glass fibre filter paper, with Gold star scintillation liquid for both water and filters.

*Table 8-27: Results for filtration with Whatman GF/F filter paper and Gold star multipurpose scintillation liquid used for counting for both water and filter papers.*

| Replicate | Water activity | Filter activity | Fraction particulate |
|---|---|---|---|
| 1 | 8224 | 10106 | 1,23 |
| 2 | 8432 | 10819 | 1,28 |
| 3 | 8323 | 10311 | 1,24 |
| Average | 8326 | 10412 | 1,25 |
| Stdev | 104 | 367 | 0,0 |
| Rstdev | 1 % | 3,5 % | 2 % |

Table 8-28 shows the results from counting of Millipore filter papers with two different scintillation liquids; Gold star multipurpose scintillation liquid and Filter Count scintillation liquid.

*Table 8-28: Results from counting of Millipore filter papers counted with Gold star multipurpose scintillation liquid and Filter Count scintillation liquid. The activities in this test are not comparable to the results in Table 8-25, Table 8-26 and Table 8-27 as it was performed at a different time with different sample, thus higher activity on the filter papers here does not mean that these filter papers catch a higher fraction of the radioactivity, as the total activity is different.*

| **Gold star multipurpose LS liquid** | **CPM** | **Filter Count LS liquid** | **CPM** |
|---|---|---|---|
| Replicate 1 | 17397 | Replicate 1 | 19095 |
| Replicate 2 | 17812 | Replicate 2 | 18358 |
| Replicate 3 | 19048 | Replicate 3 | 18194 |
| Average | 18086 | Average | 18549 |
| Stdev | 859 | Stdev | 480 |
| Rstdev | 4,7 % | Rstdev | 2,6 % |

## 8.8.4 Comments to results

### 8.8.4.1 Supor and GF filters

The repeatability of the counting of Supor® membrane filter papers seems to be quite good, with relative standard deviations 4.1 % and 5.0 % for the two different scintillation liquids used. Thus, the repeatability is good enough for use in the experiments.

The GF filter papers have a slightly lower relative standard deviation (3.5 %) even with fewer replicates, so these seem to be better than the Supor® filters. However, using the correct pore size is more important than slightly smaller uncertainty.

#### 8.8.4.2 Millipore filter papers

The Filter Count scintillation liquid totally dissolved the filter paper, gave the highest counts and the lowest relative standard deviation, thus this scintillation liquid was used when counting these filter papers. However, the TDCR values – a measure of the quenching – for this scintillation liquid was lower with 0.88 compared to 0.92 for the Gold Star. For the other filter papers above, the TDCR was always above 0.97. The water phase was not counted in this test.

## 8.9 Test of phosphate sorption to filter paper

To verify that the activity measured on the filter papers are actually associated with the particulate fraction, and not only sorbed to the filter papers, a sorption test to the 0.45 µm HAWP MF-Millipore Membrane (Cat. No. HAWP04700) and GF/F Glass Microfibre Filters from Whatman (Cat. No 1825-047, 0.7 µm) was performed. 130 mL of deionized water containing similar amount of $^{32}P$ as Part I of the water-mixing experiment and similar DRP concentration as lake water (0.36 µM) was filtered, and activity in water phase and on filter was measured. The combination of volume, activity and concentration was chosen as this would give the assumed highest fraction of sorbed activity. 5 replicates were made with each filter paper, and average sorptions of 0.36 ±0.02 % and 0.13 ± 0.01 % were seen for the glass fibre and the Millipore filter paper respectively, indicating no sorption to filter paper.

The weakness of the test is that the filtration is much quicker with deionized water than with experiment water containing particles, leaving less time for sorption of P to filter paper. Filtration time for glass fibre filter paper was generally below 30 sec in the experiment, but for the membrane filter paper it was up to 5 min. For this test the filtration times were a few seconds and < 30 sec respectively. When filtrating to make a filter paper for part II of the experiment, filtration time was about 30 min.

## 8.10 Tests to check robustness of MBM method

### 8.10.1 Time

In the MBM method, sample should be measured spectrometrically between 10-30 minutes after addition of colour-developing reagents (ISO 6878, 2004). To check how a small deviation from this will affect the result, the 4.8 µg P/L calibrations standard was left in the spectrometer cuvette and the absorbance was measured with time. After 8 minutes the absorbance is practically constant. It starts to decrease after 20 minutes, but the decrease corresponds in total to about 0.06 µM. The time interval between 10 to 30 minutes (marked by the red lines) seems to be the best, but even if the sample is measured some hours later, the change in absorbance is acceptable.

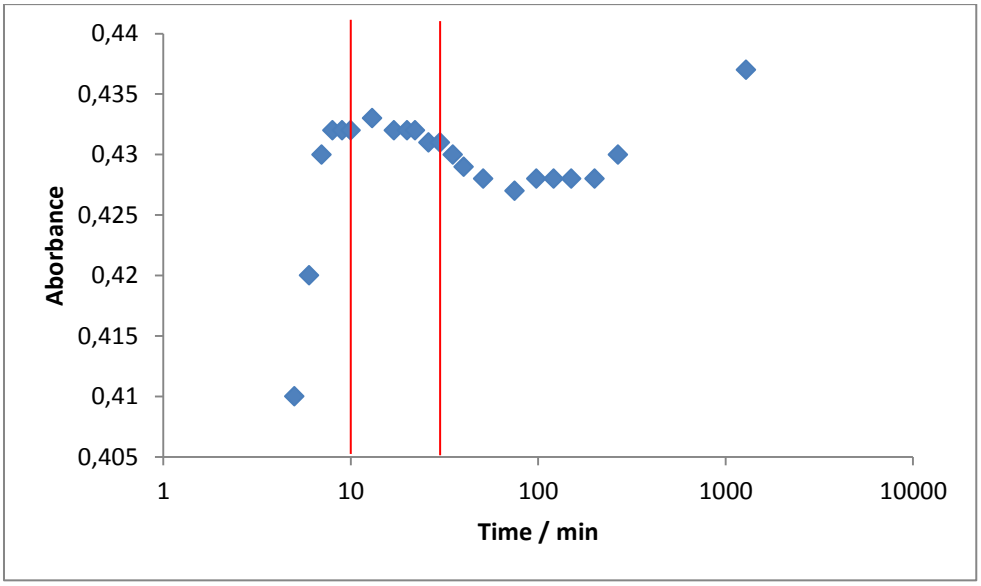


*Figure 8-14: Absorbance with time for the 4.8 µM P standard. Note the logarithmic scale of the time. The red lines mark the 10-30 min interval that is set by the ISO standard for the MBM method.*

### 8.10.2 Interferences with the MBM method

Fe affects the colour intensity when using the MBM method to measure phosphate (ISO 6878, 2004). A concentration of 10 mg/L ($0{,}3 \cdot 10^3$ µmol/L) gives less than 5 % effect on the result, thus Fe should not cause any interference in these samples (see Table 8-5). Cr and Cu also don't interfere below 10 mg/L, thus they are no problem. F is tolerable up to 70 mg/L ($4 \cdot 10^3$ µmol/L) and is also way below this (see Table 8-4). High concentrations of sulphidic sulphur

(2 mg/L) and nitrite (3.29 mg/L) also interferes, but this is assumed to be unlikely component of these water samples.

Arsenic (As) gives a similar signal as P in the MBM method (ISO 6878, 2004), and was also measured with the ICP-MS in the filtered water samples. These measurements have interference from $ArCl^+$ and are not included here. However, as 0,013 µmol/L was the highest measurement, As interference on the MBM measurements can be excluded.

Silicate concentrations up to 5 mg/L do not interfere according to ISO 6878. A concentration of 10 mg/L Si gives an absorbance corresponding to 0.16 µM. Concentrations of silicate is assumed to be below this limit.

## 8.11 Operating conditions/Instrument settings

### 8.11.1 Anion chromatography

**Apparatus and Operating conditions:**
Autosampler Dionex AS40
Anion guard Column - Dionex AG18
Anion separator column - Dionex AS 18
Anion self-regenerating suppressor - Dionex ASRS300 4mm
Detector - Dionex Conductivity Detector DS6 cell
Eluent - 28 mM KOH
ASRS – current - 70 mA
Column Temp. - 30°C
Sample loop - 25µL
Flow rate – 1.0 ml/min

All reagents and standards are made with deionized water (Milli-Q) with a resistance of 18 MΩ cm. All dishware and sample tubes are also washed with this water.

### 8.11.2 Cation chromatography

**Apparatus and Operating conditions:**

Autosampler Dionex AS40

Cation guard Column - Dionex CG16
Cation separator column - Dionex IonPac CS16 Analytical 3x250mm
Cation self-regenerating suppressor - Dionex CSRS300 4mm
Detector - Dionex Conductivity Detector DS6 cell
Eluent - 30 mM MSA

ASRS – current - 32 mA
Column Temp. - 30oC
Sample loop - 25µL
Flow rate – 0,36 ml/min

All reagents and standards are made with deionized water (Milli-Q) with a resistance of 18 MΩ cm. All dishware and sample tubes are also washed with this water.

### 8.11.3 Inductively coupled plasma optical emission spectrometry

*Table 8-29: Instrumental ICP-OES conditions used for the analysis of main cations of the water samples, and for check of the aluminium stock solution.*

| Parameter | Setting |
|---|---|
| RF power (kW) | 1.00 |
| Plasma Ar flow (L $min^{-1}$) | 15.0 |
| Auxiliary Ar flow (L $min^{-1}$) | 1.50 |
| Nebulizer Ar flow (L $min^{-1}$) | 0.75 |
| Reading time (s) | 1.00 |
| Rinse time (s) | 45 |
| Sample uptake delay (s) | 60 |
| Pump rate (rpm) | 20 |
| Number of replicates | 3 |

*Table 8-30: Wavelength selection for ICP-OES analysis*

| Element | Wavelength (nm) |
|---|---|
| Na | 588.995 |
| K | 766.491 |
| Mg | 279.553 |
| Ca | 422.673 |

### 8.11.4 Inductively coupled plasma mass spectrometry

Samples were filtrated with 0.45 µm Supor® polyethersulfone membrane filters and added 2 % v/v of 65 % $HNO_3$ Suprapur from Merck before analysis. The most abundant isotope for each element was chosen for analysis, see Table 8-31. Pb was measured by three different isotopes:

206, 207 and 208. This is an advantage, as lead in the nature occurs with different isotopic composition due to radioactive decay of other nuclides, and the concentration is more correctly calculated as an average of more isotopes, to reduce the effect of varying isotopic composition.

*Table 8-31: Overview of the chosen isotopes for the ICP-MS analysis for trace metals, according to mass number.*

| Element | Mass number |
|---|---|
| Fe | 57 |
| Al | 27 |
| Cr | 53 |
| Mn | 55 |
| Cu | 63 |
| Zn | 66 |
| As | 75 |
| Cd | 111 |
| Sn | 118 |
| Pb | 206 |
| Pb | 207 |
| Pb | 208 |

## 8.12 PHREEQC code from modelling

### 8.12.1 Keywords

Different keywords are used to define different parts of the model in PHREEQC. The use of the keywords is briefly described below.

SOLUTION is used to define which species are in the solution. This solution is in equilibrium with the surface. Input in this section is data from the Støa stream (Parekh, 2012).

SURFACE is used to define what kind of surface that is present, how much there is of it and how many weak and strong binding sites the surface has. The diffuse double layer is added to the model in this section.

SURFACE_SPECIES is used to define the sorption of different species in solution to the surface. The equilibrium constants decide to what extent the different species are sorbed, and all these different equilibriums are put in equilibrium with each other. For the HYDROUS FERRIC OXIDES surface, everything in this section is predefined in the database, and does not need to be included in the written input. For the kaolinite surface, this section is used to define how all the species in solution will sorb to the surface.

SURFACE_MASTER_SPECIES is used to define the correspondence between element names and aqueous primary and secondary master species. Normally, this data block is included in the database file and only additions and modifications are included in the input file, meaning it has to be defined for kaolinite while for the HYDROUS FERRIC OXIDES the database default is used.

SELECTED_OUTPUT is used to produce a file that is suitable for processing by R. The output that is used further is the sorbed and dissolved species of phosphate by each pH.

USER_PUNCH is used to define Basic programs that print user-defined quantities to the selected-output file. Any Basic "PUNCH" statement will write to the selected-output file. In this case, USER_PUNCH is used to get out the dissolved and sorbed phosphate species by each pH value from 1 to 14 with 0.25 pH unit steps.

USER_GRAPH is used to print a graph with the outcome every time the program is run. This graph is only used for immediate inspection of the data, and is not given in the results.

PHASES is used to define a name, chemical reaction, log $K$ , and temperature dependence of log $K$ for each gas component and mineral that can be used for speciation, batch-reaction, transport, or inverse-modelling calculations. Normally, this data block is included in the database file and only additions and modifications are included in the input file.

### 8.12.2 Sorption of phosphate on hydrous ferric oxide

```
SURFACE 1
    -equilibrate with solution 1
    Hfo_w      1         600       0.1
    Hfo_s      0.01
    -donnan 1e-008

SOLUTION 1
    temp      25
    pH        1
```

```
    pe        4
    redox     pe
    units     mmol/kgw
    density   1
    C(+4)     2.132
    Ca        1.979
    Cl(-1)    0.643
    F         0.014
    K         0.151
    Mg        0.64
    N(5)      0.189
    Na        0.39
    P(5)      0.019
    S(6)      0.708
    -water    1 # kg

SELECTED_OUTPUT
     -file stoa_hfo
     -reset false

USER_PUNCH
  10 FOR i = 1.0 to 14 STEP 0.25
  20 a$ = EOL$ + "USE solution 1" + CHR$(59) + " USE surface 1" + EOL$
  30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
  40 a$ = a$ + "   Fix_H+ " + STR$(-i) + " NaOH 10.0" + EOL$
  50 a$ = a$ + "END" + EOL$
  60 PUNCH a$
  70 NEXT i
END

PHASES
     Fix_H+
     H+ = H+
     log_k  0.0
END

SELECTED_OUTPUT
     -file stoa_hfo.txt
     -reset true
     -molalities        H3PO4       H2PO4-      HPO4-2      PO4-3
                        Hfo_wH2PO4  Hfo_wHPO4-  Hfo_wPO4-2

USER_PUNCH
 10

USER_GRAPH 1 P sorption pH
     -headings pH H3PO4 H2PO4- HPO4-2 PO4-3 Hfo_wH2PO4 Hfo_wHPO4- Hfo_wPO4-
2
     -chart_title "P adsorption on hydrous ferric oxide"
     -axis_titles pH "Moles per kilogram water"
     -axis_scale x_axis 1.0 14.8 1 0.25
     -axis_scale y_axis 1e-19 1e1 1 1 log
  -start
  10 GRAPH_X -LA("H+")
  20 GRAPH_Y  MOL("H3PO4"), MOL("H2PO4-"), MOL("HPO4-2"), MOL("PO4-3"),
MOL("Hfo_wH2PO4"), MOL("Hfo_wHPO4-"), MOL("Hfo_wPO4-2")
  -end
INCLUDE$ stoa_hfo
END
USER_GRAPH 1
     -detach
```

```
END
```